

RODRIGO FELIPE SANTOS

**EXPERIMENTAL EVALUATION OF CEMENT COMPOSITES WITH STEEL
SLAG AND ADDITION OF NANOFIBRILLATED CELLULOSE**

Thesis submitted to the Civil Engineering
Graduate Program of the Universidade Federal de
Viçosa in partial fulfillment of the requirements
for the degree of *Doctor Scientiae*.

Adviser: José Carlos Lopes Ribeiro

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“Nothing in life is to be feared, it is only to be understood. Now is the time to understand more so that we may fear less”.

(Marie Curie)

ABSTRACT

SANTOS, Rodrigo Felipe, D.Sc., Universidade Federal de Viçosa, April, 2024. **Experimental evaluation of cement composites with steel slag and addition of nanofibrillated cellulose.** Adviser: José Carlos Lopes Ribeiro. Co-advisers: José Maria Franco de Carvalho, Washington Luiz Esteves Magalhães and Leonardo Gonçalves Pedroti.

Civil construction is a sector that generates significant pollution and consumption of natural resources. However, it also has the potential to incorporate waste from various industrial sectors. Reusing waste is an interesting alternative as it reduces the amount of material deposited in inappropriate areas and the amount of raw material extracted from nature. Among the various wastes currently generated, steel slag from the steel industry can be mentioned. Characteristics such as mechanical strength and angularity of the grains favor its use as aggregate in cementitious composites. Furthermore, it has cementing properties and can be combined with Portland cement. Many studies have also demonstrated that nanofibrillated cellulose (NFC) can potentially increase the strength of cementitious matrices. In this context, the present work sought to produce and evaluate cementitious composites with steel slag aggregates, partial cement replacement by slag powder, and incorporation of NFC. This is an unprecedented association of materials, which demonstrates the relevance of evaluating their properties. To this end, a literature review was initially carried out on the effect of NFCs on cementitious materials to understand the mechanisms by which nanofibers are beneficial. Next, a study was undertaken on the impact of sonication on the dispersion of NFCs and the mechanical strength of cementitious composites produced with them. Finally, different mixtures were produced, varying the percentage of cement replacement with slag (from 0 to 50%) and the addition of NFC (from 0 to 0.2%). These mixtures were evaluated for their strength in compression and flexion, eco-efficiency, and mechanical strength after exposure to high temperatures. The literature review found that NFCs increase the hydration of the cement paste and control microcracks, enhancing mechanical strength and durability. With the experimental evaluation conducted, it was found that sonication is an efficient method for dispersing fibers, with an optimum point at which longer times impair dispersion. In the present work, the ideal time was 0.04 min/ml. As for mechanical strength, higher packing factors led to greater strength. However, very high factors impaired the performance of the composites. A packing factor of 0.72 balanced good mechanical strength and workability. In the evolution of mechanical strength over time, mixes without slag powder and with the addition of 0.2% NFC

showed an increase in flexural strength of 27.7% from 7 to 28 days, while for the mix without NFC the gain was just 11.6%. Replacing cement with slag reduced mechanical strength but increased eco-efficiency. Mixtures with 50% slag and 0.2% NFC demonstrated a 40% drop in the cement intensity in bending, indicating that a smaller amount of cement was needed to increase the strength by 1 MPa. Furthermore, 90% of this mixture's volume was waste. Finally, adding 25% powder proved to be quite efficient in mitigating the loss of mechanical strength when the temperature rises.

Keywords: Cementitious composites. Steel slag. Nanobrillated cellulose. Mechanical strength. Eco-efficiency. Behavior at high temperatures.

RESUMO

SANTOS, Rodrigo Felipe, D.Sc., Universidade Federal de Viçosa, abril, 2024. **Avaliação experimental de compósitos cimentícios com escória de aciaria e adição de celulose nanofibrilada.** Orientador: José Carlos Lopes Ribeiro. Coorientadores: José Maria Franco de Carvalho, Washington Luiz Esteves Magalhães e Leonardo Gonçalves Pedroti.

A construção civil é um setor que gera grande poluição e consumo de recursos naturais. Porém, também possui potencial de incorporar resíduos de diversos ramos industriais. O reaproveitamento de resíduos é uma alternativa interessante por diminuir a quantidade de material depositado em locais inadequados e a quantidade de matéria-prima extraída da natureza. Dentre os diversos resíduos gerados atualmente, pode ser citada a escória de aciaria proveniente da indústria do aço. Características como resistência mecânica e angularidade dos grãos favorecem o seu emprego como agregado em compósitos cimentícios. Além disso, possui propriedades cimentantes, podendo ser usada conjuntamente ao cimento Portland. Muitos estudos também têm demonstrado que a celulose nanofibrilada (CNF) possui potencial em incrementar a resistência de matrizes cimentícias. Nesse contexto, o presente trabalho buscou a produção e avaliação de compósitos cimentícios com agregados de escória, substituição parcial de cimento por escória, e incorporação de CNF. Trata-se de uma associação de materiais inédita, o que demonstra a relevância de se avaliar as suas propriedades. Para isso, inicialmente fez-se uma revisão de literatura sobre o efeito das CNFs em materiais cimentícios para compreender os mecanismos pelas quais as nanofibras são benéficas. Em seguida, empreendeu-se um estudo do efeito da sonicação na dispersão das CNFs e na resistência mecânica dos compósitos cimentícios produzidos com elas. Por fim, foram produzidos diferentes traços, variando-se a porcentagem de substituição de cimento por escória (de 0 a 50%) e de adição de CNF (de 0 a 0,2%). Tais traços foram avaliados quanto à sua resistência à compressão e flexão, ecoeficiência e resistência mecânica após exposição a altas temperaturas. Pela revisão de literatura constatou-se que as CNFs aumentam a hidratação da pasta de cimento e controlam as microfissuras, conduzindo a incrementos na resistência mecânica e durabilidade. Com a avaliação experimental conduzida, verificou-se que a sonicação é um método eficiente para dispersão das fibras, existindo um ponto ótimo a partir do qual maiores tempos prejudicam a dispersão. No presente trabalho, o tempo ideal foi de 0,04 min/ml. Quanto à resistência mecânica, maiores fatores de empacotamento conduziram a maiores resistências. No entanto, fatores muito altos prejudicaram o desempenho dos compósitos. Um fator de empacotamento

de 0,72 conseguiu equilibrar boa resistência mecânica e trabalhabilidade. Na evolução da resistência mecânica ao longo do tempo, traços sem pó de escória e com a adição de 0,2% de CNF apresentaram incremento de resistência à flexão em 27,7% dos 7 aos 28 dias, enquanto para o traço sem CNF o ganho foi de apenas 11,6%. A substituição de cimento por escória diminuiu a resistência mecânica, mas aumentou a ecoeficiência. Traços com 50% de escória e 0,2% de CNF demonstraram uma queda de 40% na intensidade do cimento na flexão, indicando que uma menor quantidade de cimento era necessária para elevar em 1 MPa a resistência. Além disso, tal traço tinha 90% do seu volume constituído por resíduo. Por fim, a adição de 25% de powder se mostrou bastante eficiente em mitigar a perda de resistência mecânica diante a elevação da temperatura.

Palavras-chave: Compósitos cimentícios. Escória de aciaria. Celulose nanofibrilada. Resistência mecânica. Ecoeficiência. Comportamento em altas temperaturas.

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CHAPTER 1: GENERAL INTRODUCTION

1.1. RESEARCH CONTEXT

Humanity has always interacted with the environment, aiming for its survival. However, over time, social organization has changed in how people interact with each other and nature. Since the Industrial Revolution, humanity has put increasing pressure on the environment, consuming natural resources intensely and bringing harmful consequences to the world. Civil construction plays a prominent role in this scenario. Considering all production at a global level, it is noteworthy that the construction sector is responsible for 50% of material consumption, 40% of energy consumption and 50% of waste production (Anink; Boonstra; Mak, 1996). Furthermore, for each ton of cement produced, the same mass of carbon dioxide (CO₂) is generated (Roy, 1999). However, despite these discouraging findings, civil construction has great potential in incorporating waste into the production of mortars and concrete (Ahmad et al., 2021). If well explored, this potential can mitigate the harmful effects generated by the sector and other sectors.

The steel industry plays a relevant role in the world economy and causes considerable environmental impacts. Wastes and co-products are generated during steel production, mainly blast furnace slag, steel slag, powders and sludge, from atmospheric control systems. (CNI, 2017). In Brazil, ten business groups responsible for 85% of the country's crude steel production generated 622 kg of co-products and waste per ton of steel produced. This corresponds to 16.6 million tons of co-products and waste generated by these groups, of which 7% (1.16 million tons) were not reused (Instituto Aço Brasil, 2020).

Considering the information presented, it becomes intuitive to incorporate waste from the steel industry in the production of cement or concrete structures in civil construction. In this way, there would be adequate waste disposal, and the demand for natural resources and the emission of CO₂ by the construction industry would be reduced. Several studies have been developed involving the use of basic oxygen furnace slag (BOFS), material from steel refining and rich in oxides of calcium (CaO), magnesium (MgO), silicon (SiO₂), and iron (FeO). After magnetic separation and time curing or a similar process, slag can be used as aggregates in the production of cementitious composites, and the results have been satisfactory (Barros et al., 2014; França et al., 2013;

Gomes et al., 2011; Hernández; Cortés; Bustos, 2015; Roslan et al., 2016; Santos et al., 2014; Tripathi; Chaudhary, 2016). Additionally, slag powders have binding properties and have been used successfully in densely packed cementitious matrices (Franco de Carvalho et al., 2019, 2020).

Recently, there has been a great appreciation of sustainable, renewable, biodegradable, non-petroleum derived materials, that pose low risks to human and animal health. This group includes cellulosic materials, especially those on a nanometric scale, such as nanofibrillated celluloses (NFCs) (Moon et al., 2011). In the literature, studies have demonstrated the efficiency of NFC in improving the mechanical properties and durability of cementitious matrices (Ardanuy; Claramunt; Toledo Filho, 2012; Fonseca et al., 2019; Goncalves et al., 2019; Mejdoub et al., 2016; Onuaguluchi; Panesar; Sain, 2014; Peters et al., 2010). However, some study gaps remain, such as the post-fire behavior of cementitious composites with NFC and the combined use of NFC and steel slag.

Thus, given the characteristics of slag and NFCs, as well as the gaps in the literature, the present research aims to (1) adopt the waste incorporation potential that the production of cementitious composites has to (2) give an adequate destination to the waste generated by the steel industry, (3) adopting renewable materials (NFCs), therefore configuring a more environmentally friendly alternative. Thus, it is expected to elucidate the impact of slag and NFCs on the mechanical strength and post-fire behavior of the composites produced.

1.2. OBJECTIVES

1.2.1. General objective

The general objective of this work is to produce eco-efficient cementitious composites using steel slag and nanofibrillated cellulose.

1.2.2. Specific objectives

To achieve and validate the proposed general objective, the following specific objectives were established:

- i. Identify the influence of sonication time on the dispersion and stability of NFCs in aqueous solution;
- ii. compare the mechanical strength of cementitious composites with steel slag aggregates and containing NFC solutions sonicated under different times, finding the optimal time;
- iii. determine the mechanical characteristics of cementitious matrices' mixtures containing steel slag aggregates and powders, with varying levels of addition of nanofibrillated cellulose and cement/slag powder ratios;
- iv. in post-fire situations, describe the mechanical behavior of cementitious matrices modified with nanofibrillated cellulose and containing powder and steel slag aggregates.

1.3. JUSTIFICATION

Themes such as global warming, consumption of natural resources, environmental preservation, and sustainability are gaining notoriety recently. Civil construction must adapt and seek ways to mitigate the impact it generates on the environment. Although it is a large consumer of energy and natural resources, the sector has an enormous capacity for incorporating waste and can take advantage of this characteristic. The steel industry, in turn, is a sector that generates a considerable portion of waste and co-products, part of which has no specific destination. In 2020, at least 1.16 million tons of waste and co-products generated in Brazil were not reused (INSTITUTO AÇO BRASIL, 2020). This is a huge quantity that is either stored or disposed in landfills, creating problems. Therefore, finding ways to reuse such waste and promote social and economic development is challenging.

Among the waste previously mentioned, this work focuses on BOFS, generated in the refining stage during the transformation of pig iron into steel through an oxygen converter process, also known as the Linz and Donawitz (LD) process. BOFS has characteristics that make it interesting for use in construction. Given its greater angularity and good mechanical strength, it can be used as an aggregate in mortars and concretes. It also has cementing properties that can be exploited. Therefore, the production of

cementitious matrices containing steel slag presents itself as a viable and sustainable solution.

In order to increase the mechanical properties of composites, NFCs can be used. Consisting of a natural material, non-petroleum derived from and non-toxic, many studies in the literature demonstrate that NFC works to control cracks and increase the mechanical properties of pastes, mortars, and concretes. This strategy of combining steel slag and NFC is unprecedented, and it could open new lines of research in civil construction and construction materials, aiming to obtain materials with greater mechanical strength and durability.

Finally, concrete structures may eventually be subject to fire. This is a drastic event, causing high human risk and economic losses. The behavior of a structural material at high temperatures must be known to guide its applicability and design. As the material developed in this work, using steel slag and NFC simultaneously is unprecedented, there are still no studies on its behavior at high temperatures.

Therefore, the combined use of steel slag and nanofibrillated cellulose has the potential to produce cementitious composites with high eco-efficiency and good performance, adding great value to them. Furthermore, the work carried out fills some gaps in the literature.

1.4. THESIS STRUCTURE

This thesis is structured into six chapters:

- (a) *Chapter 1 - General Introduction*: presents the initial considerations, objectives, and justification, highlighting the relevance of the work.
- (b) *Chapter 2 - Nanofibrillated cellulose and its applications in cement-based composites: A review*: a literature review on the production of NFCs, their characteristics, and their effects on cementitious materials.
- (c) *Chapter 3 - Influence of NFC sonication time on the performance of cementitious composites containing steel slag*: experimental investigation of the application of different sonication times in the dispersion of NFCs and the consequent impact on the mechanical properties of the cementitious composites produced.

- (d) *Chapter 4 - Mechanical performance of cementitious composites containing nanofibrillated cellulose and steel slag*: investigation of the influence of different contents of added NFC and the percentage of cement replacement by BOFS powder on the mechanical performance of cementitious composites with slag aggregate.
- (e) *Chapter 5 - Behavior of cementitious materials with steel slag and addition of nanofibrillated cellulose exposed to high temperatures*: study of the mechanical behavior of different mixtures of cementitious composites with NFC and slag subjected to temperatures of up to 600 °C.
- (f) *Chapter 6 – General conclusions*: this item highlights the main conclusions of the thesis and indicates suggestions for future work.

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CHAPTER 2¹: NANOFIBRILLATED CELLULOSE AND ITS APPLICATIONS IN CEMENT-BASED COMPOSITES: A REVIEW

Abstract: *Cellulose is an abundant and biodegradable natural material that is not derived from oil and does not harm human and animal health. With the growing demand for high-performance materials, the interest in using nanocelluloses in different areas has increased. Nanofibrillated celluloses (NFCs) are result from mechanical processing of cellulose fibers, with or without chemical pretreatments. Characteristics such as large surface area, hydroxyl groups on their surface, high mechanical strength, and high length/width ratio give NFC beneficial effects when incorporated into cement composites. This work presents a review of researches carried out in recent years in the area of cement systems incorporating NFC. The characteristics of these nanocelluloses, their production, and the effect that the nanomaterial has on the behavior of cement composites are presented. It was observed that the addition of NFC brings relevant increases in mechanical properties and has the potential to enhance the durability of the cement composites.*

Keywords: Nanofibrillated celluloses, cement composites, mechanical performance, durability, civil construction.

2.1. INTRODUCTION

Cellulose is a natural material that is found in plants and used by society for thousands of years. Even today it has a prominent role, being a raw material for fabrication of forest products, paper, textiles, among others. Besides, it has enormous environmental appeal because it is renewable, sustainable, biodegradable, not derived from oil, and implies low risks to human and animal health (Ardanuy; Claramunt; Toledo Filho, 2015; Klemm et al., 2011, 2018; Moon et al., 2011).

With the growing demand for high-performance materials, a second-generation of cellulosic products has emerged, based on the extraction of cellulose at the nanometer

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scale. In this way, defects associated with its hierarchical structure can be removed, generating high-quality products (Moon et al., 2011).

Nanocelluloses can be subdivided into three categories: bacterial nanocellulose (BNC), cellulose nanofibrils (NFCs, also called nano/microfibrillated celluloses), and cellulose nanocrystals (CNC). The first group is produced biotechnologically by bacteria; the second one is obtained by mechanical processes; and the last one is generated by chemical hydrolysis treatments (Klemm et al., 2011, 2018).

NFCs are extracted from wood (Mejdoub et al., 2016) or other plant sources, such as cotton and hemp (Lavoine et al., 2012). Nanofibrils are obtained by delamination in high-pressure homogenizers, microfluidizers, and other equipment. To facilitate the process and avoid clogging the equipment, the plant material can be pre-treated with different techniques, such as electrostatically induced swelling by charged groups, oxidative treatments (such as oxidation by the 2,2,6,6-tetramethylpiperidine-1-oxyl reagent called TEMPO), carboxymethylation, and enzymatic or mild acids treatments (Klemm et al., 2018).

It is worth mentioning the variety of terms with which NFCs are referenced in the literature. They can be called nanofibrils, microfibrils, nanofibers, microfibril aggregates, fiber aggregates, nanocellulose, microfibrillated cellulose, and nanofibrillated cellulose. However, there is a difference between the nanofibrillated cellulose (NFC) and microfibrillated cellulose (MFC) terms. The defibrillation process generates fibers with smaller diameters for NFC (between 4 and 20 nm) and larger diameters for MFC (between 10 and 100 nm). However, this difference is not always considered and both terms appear in the literature interchangeably, which may cause some confusion (Guimaraes et al., 2015; Moon et al., 2011).

Characteristics such as biodegradability, high surface area, high surface area/volume ratio, large aspect ratio, superior mechanical properties, low thermal expansion coefficient (Guimaraes et al., 2015), low density, and low price when compared to other inorganic nanofibers (Sharip; Ariffin, 2019) have aroused interest in NFC in several areas.

NFCs have innumerable applications, including reinforcement of composites, manufacture of films, packaging, barrier materials, aerosols, and biomedical products (Sharip; Ariffin, 2019). Also, they present a potential for the development of electronic components (Abdel-Karim; Salama; Hassan, 2018; Csoka et al., 2012; Hänninen et al., 2018; Rajala et al., 2016; Sheng et al., 2020).

The construction industry is responsible for 50% of the world's consumption of raw materials, 40% of energy consumption, and 50% of waste production (Anink; Boonstra; Mak, 1996). In addition, each ton of cement produced (source material for concrete structures) generates the same mass in carbon dioxide (CO₂) (Roy, 1999). These data have motivated lines of research to produce more sustainable materials. An important line of research is the production of construction materials from waste, which may be from different economic sectors, such as paper and cellulose (Carvalho Mesquita et al., 2015; Oliveira Júnior et al., 2019; Martínez-Lage et al., 2016; Novais et al., 2019; Ribeiro dos Santos et al., 2019; Santos et al., 2016, 2018; Siqueira; Holanda, 2013; Torres et al., 2017, 2020), mining (Defáveri et al., 2019; Fontes et al., 2019; Franco de Carvalho et al., 2019b, 2020; Ince, 2019; Mendes et al., 2019; Siddique; Jang, 2020), ornamental stones production (Amaral et al., 2019; Lemes et al., 2017; Mundra; Agrawal; Nagar, 2020; Mymrin et al., 2020; Pedroti et al., 2012, 2014; Salgado Lopes et al., 2019; Tressmann et al., 2020; Yang et al., 2020), paints (Almesfer; Ingham, 2014; Ribeiro et al., 2016; Said et al., 2016), steel industry (Kalpana; Tayu, 2020; Rubio-Cintas et al., 2019; Subathra Devi et al., 2019; Wang et al., 2020) and even civil construction (Bahrami et al., 2020; Kox et al., 2019; Medeiros et al., 2019; Puente de Andrade et al., 2020; Shi et al., 2018). Another possible line of research is the use of more sustainable materials to obtain products with improved quality. In this case, nanofibrillated celluloses have shown promising results in cement composites, with increases in stiffness (Fonseca et al., 2019), compression strength (Mejdoub et al., 2016), tensile strength (Onuaguluchi; Panesar; Sain, 2014), fracture energy (Peters et al., 2010), behavior at higher temperatures (Hoyos et al., 2019), and durability (Goncalves et al., 2019) being reported.

Some papers have reported a general overview of cement composites containing conventional short and pulp fibers from plant sources (Ardanuy; Claramunt; Toledo Filho, 2015; Onuaguluchi; Banthia, 2016). Other papers concentrated on nanosized admixtures and reviewed the application of nanocelluloses on films, papers, biomaterials, and reinforced composites in general (Azizi Samir; Alloin; Dufresne, 2005; Klemm et al., 2011, 2018; Lavoine et al., 2012; Moon et al., 2011; Sharip; Ariffin, 2019; Wang et al., 2019). The application of different types of nanocelluloses (e.g. NFC, BNC, CNC) in cementitious composites has been reviewed by Balea et al. (2019), Bhalerao et al. (2015), Fu et al. (2017), and Lee et al. (2019). All of them mainly focused on the effects of these nanocelluloses on mechanical and rheology properties. Although a large amount of research progress has been made on NFCs, there is no review paper focused on using this

type of nanocellulose in cementitious composites in a more specific way. In addition, the recent concern about the durability of concrete structures suggests the need for a detailed overview of durability properties of NFCs-based composites at this time. Therefore, the high number of published articles dealing with NFC-based cement composites calls for a critical investigation of the current state-of-the-art. This paper presents a detailed overview of recent advances of existing research on the effects of NFCs on cement-based materials, with emphasis on their mechanical performance and durability.

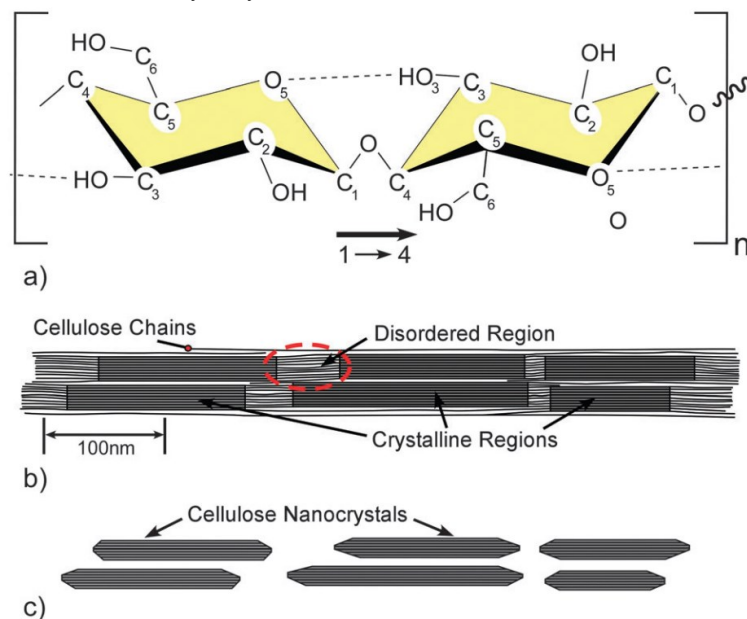
At first, a background focused on definitions, characteristics, fabrication, and potential applications of nanofibrillated cellulose was presented. The paper also provides the reader with descriptions and comparisons of mechanical and durability properties of cement-based composites containing NFCs. Details about the interaction between these nanofibers and the cementitious matrix were also covered. Finally, discussions on the behavior of NFCs in alkaline environments were provided.

2.2. STRUCTURE, PRODUCTION, AND APPLICATIONS OF NANOFIBRILLATED CELLULOSE

Cellulose is considered the most abundant organic material on the planet, with wood being its main source. It is also found in plant fibers, such as cotton, hemp, and flax, in marine animals (tunicates), algae, fungi, invertebrates, and bacteria. Even with diversified sources, the corresponding celluloses presents common characteristics, e.g. white fibers-like structure, absence of odor, and density of around 1.5 g/cm^3 (Lavoine et al., 2012).

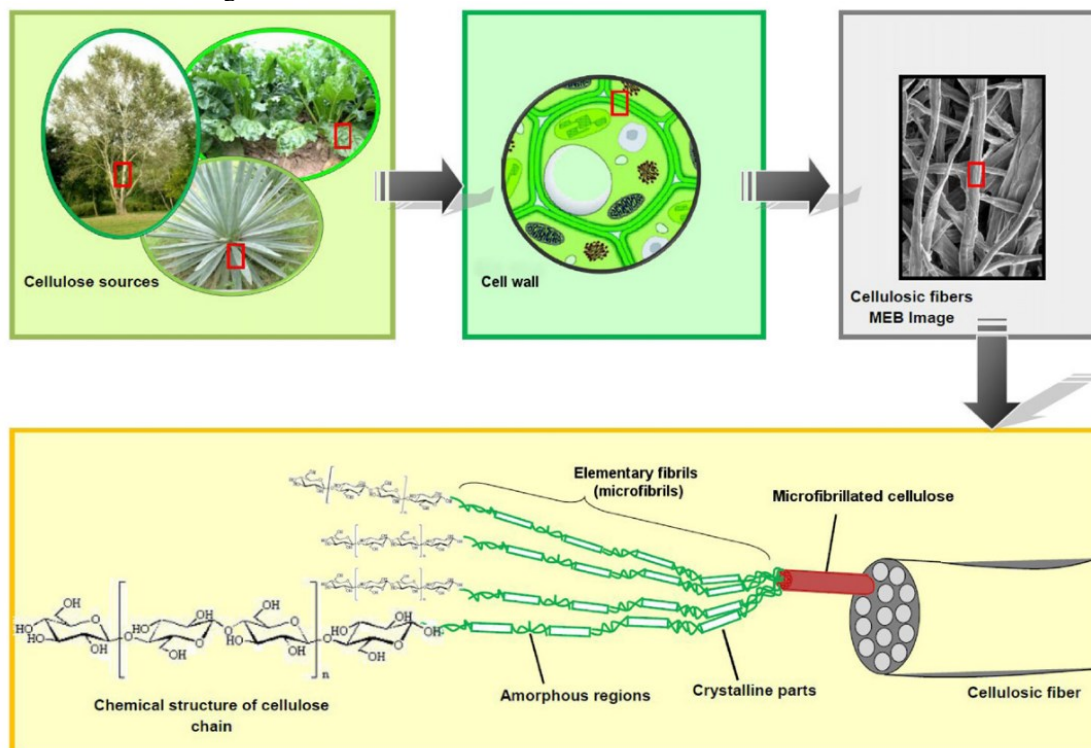
The cellulose structure consists of a linear chain whose basic unit is two molecules of anhydroglucose ($\text{C}_6\text{H}_{10}\text{O}_5$), linked together through an oxygen atom covalently bonded to C1 of a glucose molecule and C4 of the adjacent molecule, as shown in Figure 1a. This bond is called β -1-4 glycosidic and the basic unit mentioned can be repeated from 10,000 to 15,000 times. Besides, hydrogen bonds between hydroxyl groups and oxygen from adjacent glucose molecules stabilize the linear cellulose chain. Different chains interact with each other through hydrogen bonds and van der Waals forces forming microfibrils (or elementary fibrils). These microfibrils are associated in microfibrillated celluloses (also called nanofibrillated celluloses), and finally constitute the fibers of cellulose, as represented in Figure 2 (Azizi Samir; Alloin; Dufresne, 2005; Klemm et al., 2018; Lavoine et al., 2012; Moon et al., 2011).

Figure 1 - Schematics of (a) a single cellulose chain repeat unit, (b) crystalline and amorphous regions of nanofibrillated celluloses that compose a cellulose fiber, (c) cellulose nanocrystals from acid hydrolysis of cellulose fibers.



Source: Moon et al. (2011).

Figure 2 - Schematics of cellulose from its source to its molecular structure.



Source: Lavoine et al. (2012).

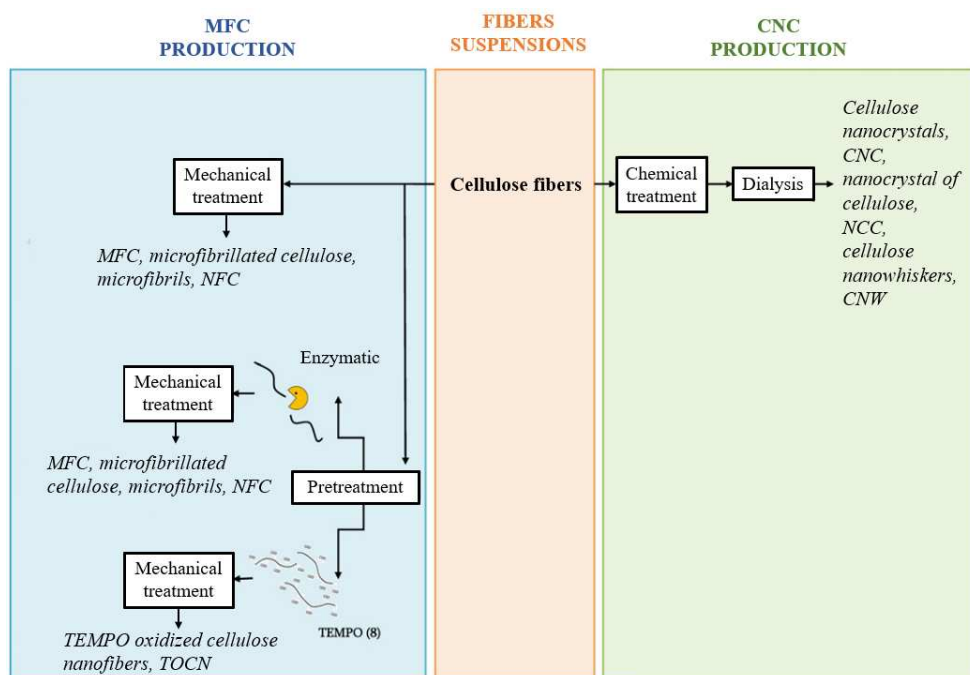
Elementary fibrils have a length of several micrometers and diameters around 5 nm, which can vary from 2 to 20 nm depending on the cellulose source. On the other hand, nanofibrillated celluloses (NFCs) have diameters between 20 to 50 nm (Klemm et

al., 2018; Lavoine et al., 2012), which are responsible for the stiffness and strength of cellulose fibers (Börjesson; Westman, 2015).

NFCs have crystalline and amorphous regions, as shown in Figure 1b. The crystalline regions are composed of cellulose chains that are aggregated due to a complex network of hydrogen bonds and van der Waals forces, which is responsible for their stabilization. The amorphous regions result from changes in the aggregation process that lead to defects in the structure (Habibi; Lucia; Rojas, 2010; Lavoine et al., 2012). These amorphous regions can be removed by acid hydrolysis, resulting in cellulose nanocrystals (Eyley; Thielemans, 2014), which are shown in Figure 1c.

Figure 3 shows the preparation of CNC and NFC. While CNCs are produced via controlled acid or enzymatic hydrolysis, NFCs are produced through mechanical defibrillation (Lavoine et al., 2012).

Figure 3 - Production of nanofibrillated cellulose and cellulose nanocrystals.



Source: Adapted from Lavoine et al. (2012).

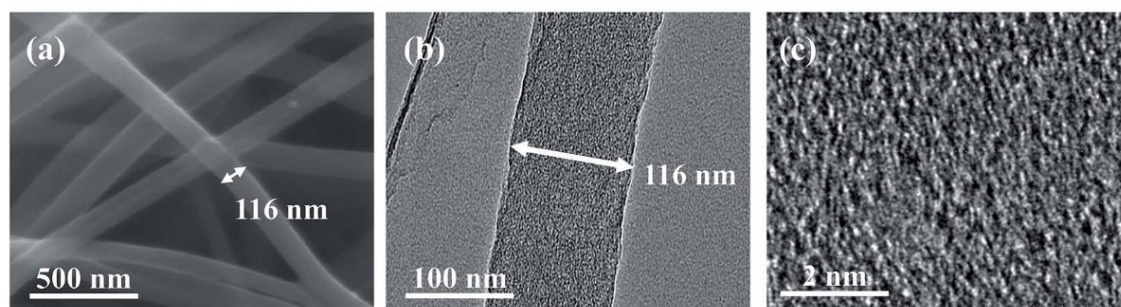
The mechanical treatment of cellulose for NFC production involves physical processes under high pressure, capable of defibrillating the fibers and separating them into nanometric fractions (Wang et al., 2019). There are different types of delamination equipment used for mechanical treatment, such as high-pressure homogenizers or microfluidizers, ball mills, common refiners, steam explosion, ultrasonication, high-speed blenders, and others (Klemm et al., 2018).

However, NFCs obtained only by mechanical treatment demand a greater amount of energy and favor the clogging of the equipment used (Klemm et al., 2018), in addition to generating fibers of larger sizes and with non-homogeneous distributions. For this reason, it is common to pre-treat the raw material before mechanical processing, through acid prehydrolysis, enzymatic prehydrolysis, alkaline treatment, oxidative treatment, and other processes (Wang et al., 2019).

According to Balea et al. (Balea et al., 2019), the NFC market is growing over the world, but has some shortcomings, especially those related to high-volume applications and cost-competitiveness with traditional technology. Recently, many companies have successfully developed strategies focused on improving energy-efficiency, up-scalable production methods, and reducing production costs of NFCs. However, the successful establishment of the market of the nanocellulose-based products requires investment and the development of new research, laboratory to pilot-scale strategies, and a technological platform (Mishra; Shanker; Khare, 2020). In the short term, the production of NFCs in large quantities and lower cost will open up possibilities for the high-volume applications required by the construction, automobile, paper, adsorbent, textile, and hygiene sectors (Balea et al., 2019; Mishra; Shanker; Khare, 2020).

In terms of geometry, NFCs have a high surface area, a high area/volume ratio, and a high length/width ratio (Guimaraes et al., 2015). Figure 4a shows the linear geometry of NFCs, and Figure 4b and c shows a detail of a nanofibril.

Figure 4 - (a) Scanning electron microscopy, (b) transmission electron microscopy, and (c) high-resolution transmission electron microscopy images of NFC.



Source: Xiao et al. (2018).

They also have a low thermal expansion coefficient (Fukuzumi et al., 2009) and high mechanical properties, with elasticity moduli ranging from 65 GPa to 150 GPa (Cheng; Wang, 2008; Cheng; Wang; Harper, 2009; Iwamoto et al., 2009; Josefsson,

2015). This allows NFCs to be used in the production of films for gas barriers (Belbekhouche et al., 2011; Fukuzumi et al., 2009), nanopapers (Malucelli et al., 2018, 2019), packaging material (Jin et al., 2021; Missio et al., 2018; Pacaphol; Seraypheap; Aht-Ong, 2019), and reinforcement of composites (Do Lago et al., 2020; Kumode et al., 2017; Travalini et al., 2019; Wu et al., 2019; Zhang et al., 2020; Zhao et al., 2014) and papers (Balea et al., 2016). Another relevant feature is their electrical properties, with potential use in the production of piezoelectric sensors (Abdel-Karim; Salama; Hassan, 2018; Csoka et al., 2012; Hänninen et al., 2018; Rajala et al., 2016) and lithium batteries (Sheng et al., 2020) from renewable sources and at lower costs.

Another application of NFCs is in the production of biomaterials, i.e., synthetic or natural materials that maintain contact with tissues, blood, and biological fluids as prostheses, diagnostics, therapies, and storage applications without affecting the organism and its components (Bruck, 1980). NFCs are applied in drug transport systems (Kolakovic et al., 2011; Valo et al., 2011), in 3D cell cultures (Bhattacharya et al., 2012), in orthopedic (He et al., 2018; Kamel et al., 2020), ophthalmic (Tummala et al., 2017) and dental (Silva et al., 2016) applications, in biosensors for diagnostics (Orelma et al., 2012a, 2012b), wound dressing (Aliabadi et al., 2020; Claro et al., 2020) and antibacterial films (Martins et al., 2012). BNC has been used in the production of cardiovascular equipment (Fink et al., 2011; Malm et al., 2012; Schumann et al., 2009), which demonstrates the potential application of NFC for the same purpose. Other applications include NFCs as food additives in the food industry (Andrade et al., 2015; Parés et al., 2018; Wang et al., 2018; Yu et al., 2021), and as pesticide releasers in the agriculture sector (Mattos; Magalhães, 2016; Xiao et al., 2021).

Finally, NFCs have been incorporated in cement-based composites and provided mechanical and durability gains (Fonseca et al., 2019; Goncalves et al., 2019; Hoyos et al., 2019; Onuaguluchi; Panesar; Sain, 2014; Peters et al., 2010). In addition, the benefits of the large-scale application of natural fibers for the production of cement-based composites are immense in terms of environmental, energy and resource conservation (Onuaguluchi; Banthia, 2016). This line of investigation and application will be better described in the next topics.

2.3. APPLICATIONS OF NFC IN CEMENT-BASED COMPOSITES

2.3.1. Research involving the addition of NFC in cement-based materials

The addition of NFC in cementitious matrices aims to improve the performance of cement-based composites through the use of more sustainable materials. The most expressive works in the area started to appear in 2010, which demonstrates how recent this line of research is. Table 1 presents an exhaustive list of studies already carried out in the area, from which the approaches adopted by different authors can be analyzed.

Different cementitious matrices have been evaluated, from the most traditional (paste, mortar, concrete) to oil well cement and extruded cement. It demonstrates that the studies conducted have sought to evaluate the influence of NFC in composites for different types of applications. It is also possible to realize how diverse the source of cellulose can be. In addition to eucalyptus and pine woods, fibers from sisal, bamboo, apple, jute, and fique have been incorporated in cement-based materials. This variety of sources is interesting because it allows the production of NFC to adapt to the different realities of each community, favoring local development, and possible reduction in production costs.

The diameters of the fibers range from 5 to 500 nm and the contents of NFC in the matrices are low, being below 5% by cement weight. Given the intrinsic water retention by NFC (Ferrara et al., 2015; Hisseine et al., 2020), there is a tendency to use superplasticizers for the production of mortars and concretes. The superplasticizer content varies between the different studies, and may be associated with the differences between the materials used and the desired water/cement ratio. It is also worth mentioning that some works have applied a pre-treatment of fibers, such as acid, alkaline, and TEMPO-oxidation processes. However, such techniques are not mandatory, as indicated in Table 1.

The addition of NFC in cementitious matrices promotes gains in mechanical performance and durability, which will be discussed in detail in the subsequent sections.

Table 1 - General characteristics of different research involving NFC in cement-based materials.

(to be continued)

Matrix	Characteristics of NFC			NFC content ^(a)	Water reducer content ^(b)	Dispersion methods of NFC in the composites	Water / cement ratio (by mass)	References
	Source	Special pre-treatment	Width (nm)					
Concrete	Wood	-	-	0 to 5	1.6	Mixer	0.22 to 0.35	(Peters et al., 2010)
Concrete	-	-	-	0 to 0.25	4.0	Mixer	0.23	(Machado et al., 2016, 2017)
Mortar	Eucalyptus pulp	-	20-50	0 and 0.025	5.5	Mixer	0.31 to 0.33	(Ferrara et al., 2015)
Paste	-	TEMPO oxidation	20-100	0 to 0.40*	-	Magnetic stirrer and supersound process	0.35	(Dai et al., 2015)
Paste	-	-	5-10	0 to 0.40	Maximum of 1.6	Ultrasonic bath and mixer	0.5	(Onuaguluchi; panesar; sain, 2014)
Paste	Eucalyptus pulp	TEMPO oxidation	5-10	0 to 0.50	-	Ultrasonic bath and mixer	0.26	(Mejdoub et al., 2016)
Oil well cement paste	Wood pulp	Acid treatment	20	0 to 0.28	-	Mixer	0.38	(Sun et al., 2016)
Paste	Fique	KOH-5 treatment	Below 100 nm mostly	0 to 0.40	-	Mixer	0.45	(Hoyos et al., 2019)
Paste	-	-	25-500	0 to 0.80	0.2	Sonicator and mixer	Variable	(Claramunt et al., 2019)
Paste	Wood pulp	TEMPO oxidation	10-20	0 to 1.5	0 to 0.91	-	0.485	(Bakkari et al., 2019)
Concrete	Apple	-	2.68	0 to 1.0	-	Mixer	0.45	(Barnat-hunek et al., 2019)
Paste	Pine sawdust	-	28	0 to 2.0	~1.3	Mixer	~0.34	(Reixach et al., 2019)
Mortar	Sisal pulp	-	25-250	3.3	Maximum of 4.0	Mixer	0.67	(Ardanuy et al., 2012)
Mortar	Sisal pulp	-	25-250	0 to 4.0	Maximum of 4.0	Mixer	0.50 to 0.70	(Ardanuy; Claramunt; Toledo Filho, 2012)
Extruded cement mortar	Bamboo pulp	-	16.2	1.3	1.3	Mixer	0.57	(Correia et al., 2018)
Extruded cement mortar	Jute	NaOH treatment	-	0 to 3.05	1.0	Mixer	0.61 to 0.64	(Fonseca et al., 2019)
Mortar	-	-	10-50	0 to 1.29	0 to 0.052	Mixer	0.485	(Goncalves et al., 2019)

Table 1 - General characteristics of different research involving NFC in cement-based materials.

(conclusion)

Matrix	Characteristics of NFC			NFC content ^(a)	Water reducer content ^(b)	Dispersion methods of NFC in the composites	Water / cement ratio (by mass)	References
	Source	Special pre-treatment	Width (nm)					
Paste	Wood	TEMPO oxidation	50-90	0 to 0.40	-	Magnetic stirrer, sonicator and mixer	0.35	(Jiao et al., 2016)
Paste	-	-	5-20	0 to 4.5	-	Magnetic stirrer and mixer	0.5, 1, 2 and 3	(Zhang; scherer, 2020)
Mortar	Sisal pulp	-	25-250	0 to 8.0	Maximum of 4.0	Mixer	0.56 to 0.69	(Claramunt; Ardanuy; Fernandez-Carrasco, 2015)
Paste	Bamboo pulp	-	10-20	Sheets of pulp 1.0**	-	Mixer	2	(Correia et al., 2019)
Paste	Eucalyptus pulp	-	-	-	-	Mixer	-	(Correia; Santos; Savastano Júnior, 2015)
Oil well cement paste	-	-	-	0 to 0.15	-	Magnetic stirrer and mixer	0.50	(Tang et al., 2019)
Paste	Soft wood pulp	Without treatments, coating with silica nano-particles	20-500	0 and 0.1	-	Conventional and/or high shear mixer	0.35	(Kamasamudram; Ashraf; Landis, 2020)

Notes:

(a) All of the NFC contents were presented in terms of weight of cement, except for those presented in Dai et al. (2015) (marked with a *, as they were provided in terms of volume of composite) and Correia; Santos; Savastano Júnior (2015) (marked with a **, as they were provided in terms of weight of particulate raw materials).

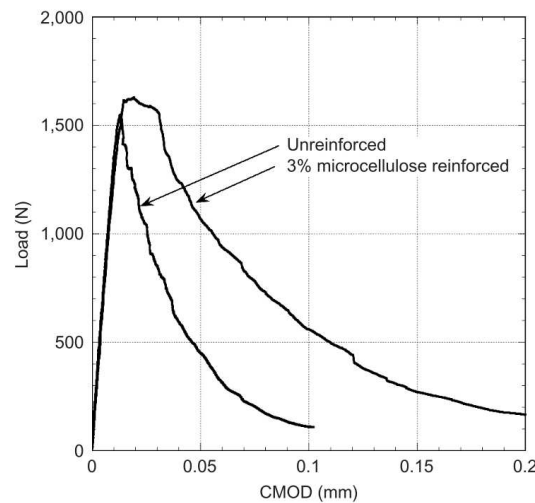
(b) All of the contents of water reducer agents were presented in terms of weight of cement.

Source: The author (2021).

2.3.2. Effects on mechanical strength

NFCs have been used successfully in cement-based composites, promoting increases in mechanical properties. Peters et al. (2010) used commercial NFC (Sigmacell 101) for the production of reactive powder concrete (RPC). The NFC contents were 1%, 3%, and 5% by weight of cement. For the reinforcement of 3% of fibers, there was a small increase in the tensile strength and an increase of 50% in the fracture energy when compared to the non-reinforced material (Figure 5).

Figure 5 - Load–deformation curve of samples with and without NFC reinforcement.



Source: Peters et al. (2010).

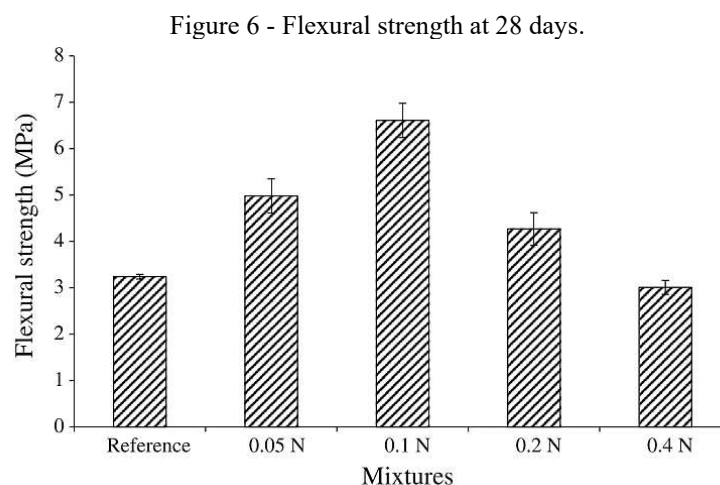
Machado et al. (2016, 2017) also produced RPC with NFC, but with lower contents of nanofibers (0.10%, 0.20%, and 0.25% by weight of cement). The results of the modulus of elasticity, compressive, and shear strength did not present significant differences according to Tukey's test. In terms of flexural strength, there was a reduction in the series with 0.20% NFC, in comparison to the RPC without NFC. Since the amount of water and superplasticizer were kept constant in all series, the authors noted that greater additions of NFC diminished the RPC's workability and jeopardized the concrete compaction.

Stephenson (2011) added NFC contents of 0.1, 0.5 and 1.0% (by weight of cement) in ultra high performance concretes and observed that the 0.5% NFC provided the greatest gains in fracture properties and significantly reduced the shrinkage at the initial ages of the composites. In their preliminary studies, Ferrara et al. (2015) also

observed a reduction in autogenous shrinkage when a NFC content of 0.025% (by weight of cement) is incorporated in mortar. This reduction was attributed to the extra amount of water absorbed by the cellulose fibers, favoring the internal curing process.

Dai et al. (2015) used NFC with diameters between 20 and 100 nm in cement pastes (concentrations from 0.10% to 0.40% by volume of cement). They observed that mixtures with additions of 0.15% NFC by volume of cement and water-cement ratio of 0.50 provided increments of 20% in compressive strength, and 15% in flexural strength.

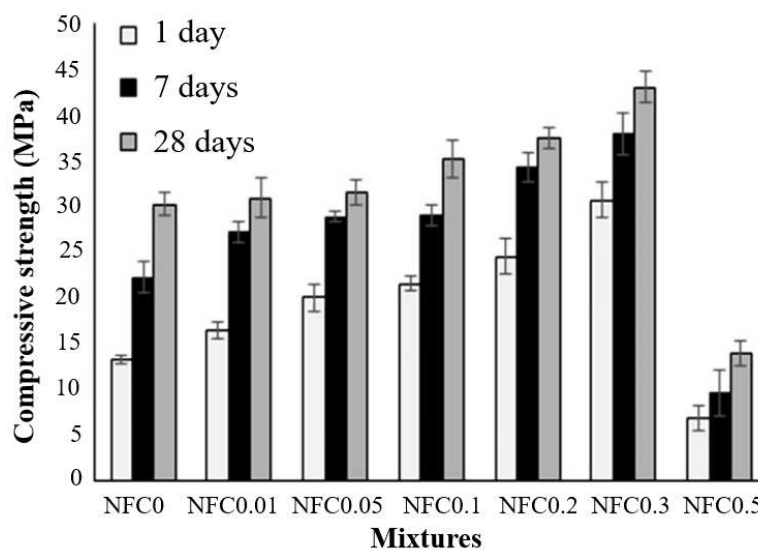
Onuaguluchi, Panesar, and Sain (2014) used NFC with diameters from 5 to 10 nm and general use limestone (GUL) cement to produce cement pastes. The contents of NFC were 0.05%, 0.1%, 0.2% and 0.4% by weight of cement. The most significant increase in flexural strength (106%) was observed for the addition of only 0.1% NFC (Figure 6).



Source: Onuaguluchi; Panesar; Sain (2014).

Mejdoub et al. (2016) undertook a study of the thermal, mechanical, and microstructural properties of pastes with the addition of NFC. The cellulose fibers were submitted to a TEMPO-mediated oxidation pre-treatment to facilitate defibrillation and ameliorate the NFCs dispersion within the cement matrix. The diameters obtained varied from 5 to 10 nm, as those obtained by Onuaguluchi, Panesar, and Sain (2014). The NFC concentrations in the pastes were 0.01%, 0.05%, 0.1%, 0.2%, 0.3%, and 0.5% by weight of cement. The addition of 0.3% of NFCs provided a denser matrix with lower porosity. Therefore, the highest increase in compressive strength (43%) was observed with the addition of 0.3% NFC (Figure 7).

Figure 7 - Compressive strength of different mixtures of cement pastes with NFC.



Source: Mejdoub et al. (2016).

Sun et al. (2016) added NFC concentrations ranging between 0.04% and 0.28% (by weight of cement) to oil well cement pastes and observed that the 0.04% NFC content provided the highest flexural strength increase to the control specimens (20.7%).

Hoyos et al. (2019) studied the addition of NFC in low-alkali cement. The process of NFC production generated a small number of fibers with diameters above 100 nm and the largest amount with diameters below 100 nm. The levels of addition of NFC in cement pastes were 0.1%, 0.2%, 0.3% and 0.4% by weight of cement. A higher degree of hydration was observed in the mixtures containing 0.4% of NFC.

Claramunt et al. (2019) evaluated the effect of adding different NFC and CNC contents (ranging between 0.1% and 0.8% by weight of cement) on calcium aluminate cement (CAC) and ordinary Portland cement (OPC) matrices. The diameters of NFC varied from 25 to 500 nm and those of CNC range from 25 to 500 nm. The authors found highest improvements (28%) in flexural strength for small additions of 0.1% and 0.2% of nanocelluloses.

Bakari et al. (2019) produced NFC from wood pulp with diameters between 10 and 20 nm from the TEMPO-mediated oxidation pre-treatment and defibrillation. The addition of NFC concentrations ranging from 0.125% to 1.5% (by mass of cement) proved to be beneficial in mitigating dimensional changes and cracks related to the shrinkage of cement pastes.

The effects of cellulose nanofibrils from apple cellulose on concrete mechanical properties were also evaluated by Barnat-Hunek et al. (2019). When NFC contents of

0.5% and 1.0% (by mass of cement) were used, the concrete compressive strength increased by 2.1% and 23.3%, respectively, while the concrete flexural strength increased by 12.0% and 34.5%, respectively.

Reixach et al. (2019) produced cement pastes containing different contents (0.0%, 0.5%, 1.0%, 1.5%, and 2.0% by weight of cement) of lignocellulosic micro/nanofibers with diameters about 28 nm. Specimens were tested for flexural strength at 7, 14, and 28 days. The authors observed improvements in flexural strength for all the dosages analyzed. The higher increases (~ 25%) occurred for concentrations of nanofibers of 1.0% and 1.5%, at 28 days curing.

Studies with cellulose filaments (CF), a material similar to NFC but with longer lengths, also show interesting results, with gains in compressive, flexural, and splitting-tensile strengths, and in energy absorption (Hisseine et al., 2018, 2019; Hisseine; Omran; Tagnit-Hamou, 2018). Nanoscale cellulose filaments with diameters ranging between 30 and 400 nm affect the mechanical performance of ultra-high performance concretes. According to Hisseini et al. (2020), lower CF contents (0.15% of the cement mass) resulted in an enhancement in compressive and flexural strength of up to 10%, while higher CF contents (0.30%) adversely affected the compressive strength, particularly at earlier ages (1 and 7 days), and did not significantly affect the flexural strength.

The potential application of different kinds of NFC (pure NFC, silica coated NFC, and lignin-containing NFC) for improving the mechanical performance of cement pastes was recently investigated by Kamasamudram, Ashraf and Landis (2020). A constant concentration of 0.1% (by weight of cement) of NFC was used in all of the case scenarios. Pure NFC and lignin-containing NFC had very little effect on the 90-days compressive strength of the cement pastes, while a 13% strength increase was provided by the silica coated NFC. In addition, pure NFC provided flexural strength increases up to 70%, followed by lignin-containing NFC (increases up to 40%). However, silica coated NFC did not have any significant benefit on the flexural strength of the cement pastes.

Regarding the length of the fibers, some studies have shown that the partial replacement of natural fibers (with greater lengths) by NFC promotes gains in flexural strength and stiffness. For example, Ardanuy et al. (2012) observed that the flexural strength and flexural modulus of NFC-reinforced mortars were about 36% and 71% higher than those of mortars reinforced with conventional cellulose sisal fibers. However, the nanomodified mortars exhibited a brittle failure mode. According to Balea et al.

(2019), it happens because the NFCs' capacity for incipient macrocracks bridging is low, due to their small size.

Correia et al. (2018) compared the performance of extruded cement-based composites containing 9% of bamboo pulp and composites containing 8% of bamboo pulp associated with 1% of NFC (percentages in relation to the total dry mass content). They found that samples with 1.33% of NFC (by weight of cement) provided increases of 34% in flexural strength, 13% in fracture toughness, 7% in fracture energy, and 5% in modulus of elasticity of the cement composites, considering a curing period of 28 days.

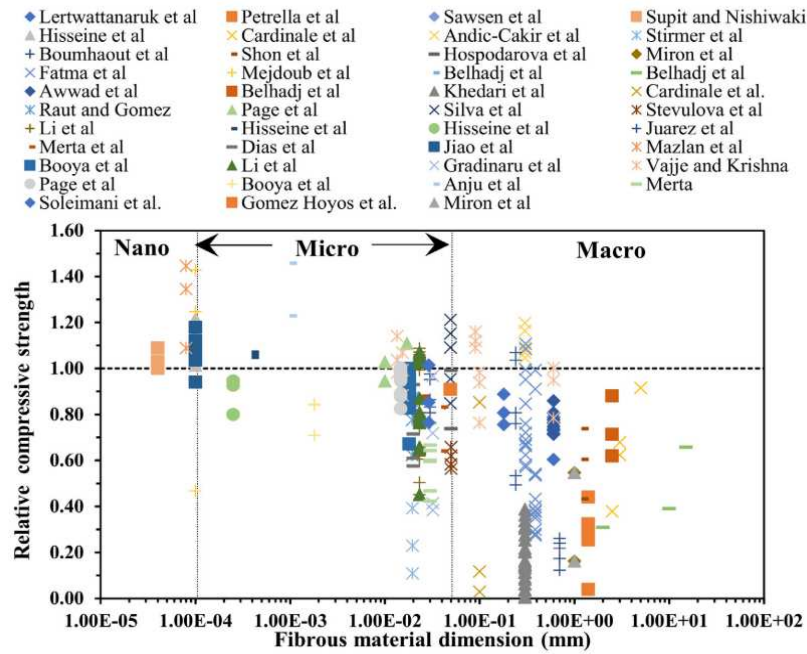
Fonseca et al. (2019) used NFC in the production of extruded cement-based composites. Mixtures with 0.73%, 1.47%, and 3.05% NFC by weight of cement were compared to mixtures with the same proportions of jute fibers (3 mm length). In general, formulations reinforced with 3.05% of NFC presented the best mechanical performance. Increases of 28% in the limit of proportionality, 32% in the modulus of rupture, and 192% in the toughness average values were observed for this NFC content.

Finally, Pedroso and Flores-Colen (2020) recently conducted an exhaustive data gathering related to incorporating organic fibers in cementitious materials. Through a statistical approach, they concluded that the greatest gains in compressive strength occur for fibers with dimensions between 50 nm and 1000 nm (Figure 8). In addition to small dimensions, the percentage of fiber additions should be lower, in the range of 0.03% to 0.40% of the total volume (Figure 9). In these situations, the average compressive strength increases range between 5% and 30%. Thus, this work and the others cited previously demonstrate better mechanical performance of cementitious composites produced with nanofibers compared to fibers with larger dimensions.

The studies reviewed in this section indicate that the mechanical properties of cement-based composites with NFC contents ranging between 0.01% and 5.00% (by mass of cement) had been already investigated. The lowest NFC concentration was 0.01% (by mass of cement), which caused a slight decrease in the porosity of cement-based materials, leading to a negligible enhancement in their compressive strength. However, an analysis of the experimental results indicates that the value of various mechanical properties (e.g., compressive strength, tensile strength, flexural strength, modulus of elasticity, among others) tend to increase with the increase in the NFC content, although excessive NFC dosage will decrease the mechanical performance of the cement-based composites due to inhomogeneous dispersion and detrimental agglomeration of nanomaterials. This literature overview indicated that the highest level of NFCs sustained

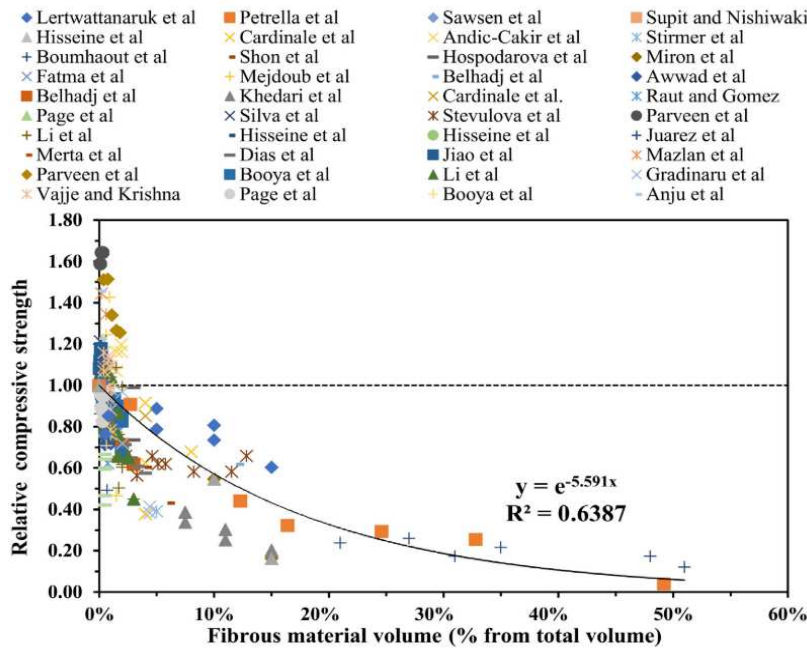
by cement-based materials was 5.00% (by mass of cement), although this NFC content was found to often lead to an inappropriate workability.

Figure 8 - Relationship between relative compressive strength and fibers dimension.



Source: Pedroso; Flores-Colen (2020).

Figure 9 - Relationship between relative compressive strength and the percentage of fiber additions.



Source: Pedroso; Flores-Colen (2020).

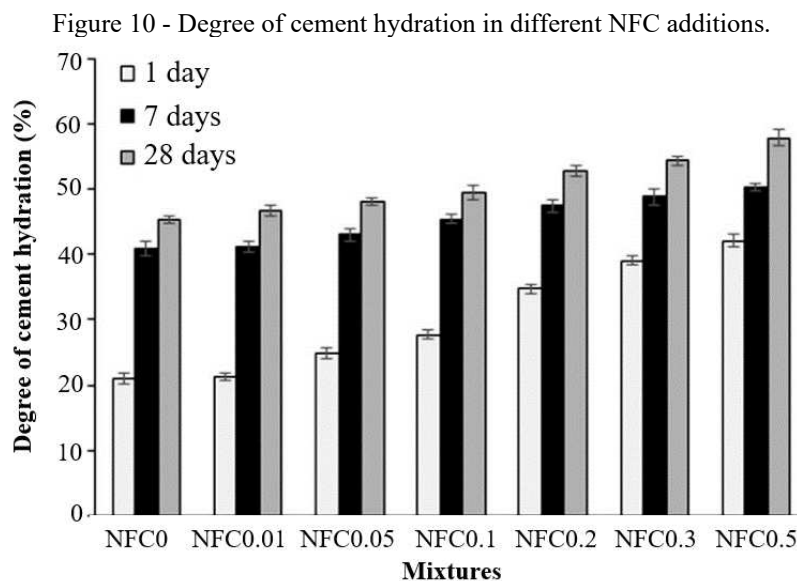
The experimental works reported optimum mechanical properties being achieved when the NFC concentration is within the range between 0.10% and 3.00% (by mass of cement). The main reasons leading to the distinct optimum NFC contents reported in these studies are the different mix proportions, NFC characteristics, methods of dispersion of NFCs, type and concentration of dispersing agents, and properties of the raw materials used to produce the cement composites. This review indicated that the most significant mechanical improvements provided by NFC were increases of 43% in compressive strength, 106% in flexural strength, 5% in modulus of elasticity, 71% in flexural modulus, 50% in fracture energy, and 192% in toughness. A detailed overview of the mechanisms behind these improvements is presented in the next section.

2.3.3. Interaction between cellulose nanofibrils and cementitious matrices and effects on mechanical properties

This section deals with the potential interaction mechanisms of NFCs incorporated in cement matrices. The studies mentioned in the previous section indicated that NFCs positively impact the mechanical strength of cementitious materials. From microstructural observations, such performance can be attributed to greater hydration in the matrices, as pointed out by Mejdoub et al. (2016), Onuaguluchi, Panesar, and Sain (2014), Hoyos et al. (2019), and Dai et al. (2015). NFCs act as nucleation sites, inducing a faster hydration process. Thus, the hydration degree and the formation of hydrated products, such as portlandite, ettringite, and C-S-H, tend to increase according to the NFC content (Mejdoub et al., 2016). Figure 10 shows that the degree of cement hydration increases with the increase in the NFC content of the mixtures.

Hoyos et al. (2019) observed C-S-H crystals growing in and around NFCs using the water retained by the nanocellulose. The authors attributed this fact to the short-circuit diffusion mechanism (SCD) proposed by Cao et al. (2015) when studying the addition of CNC in cementitious matrices. This mechanism is shown in Figure 11. During curing, hydrated products (C-S-H) form a shell around the cement particle that slows down the hydration inside the particle (Figure 11a). When there is CNC in the paste, they adhere to the cement particles and form a water transport channel into the unhydrated particle. This would collaborate, therefore, for better hydration of the matrix (Figure 11b). Although this mechanism has been proposed for cellulose nanocrystals, some authors who have used NFC in cementitious matrices have defended it as an explanation for the greater

hydration observed in cement-based composites (Bakkari et al., 2019; Goncalves et al., 2019; Hoyos et al., 2019). For instance, Santos et al. (2017) explain that NFCs adhere to the cement particles, remain in the hydration product shell, form a path to transport water to the unhydrated cement core, and facilitate a larger portion of cement reacting. Actually, recent findings of Tang et al. (2019) indicated that CNF provided higher gel strength increases to cement pastes than CNC, due to the longer lengths of CNF.



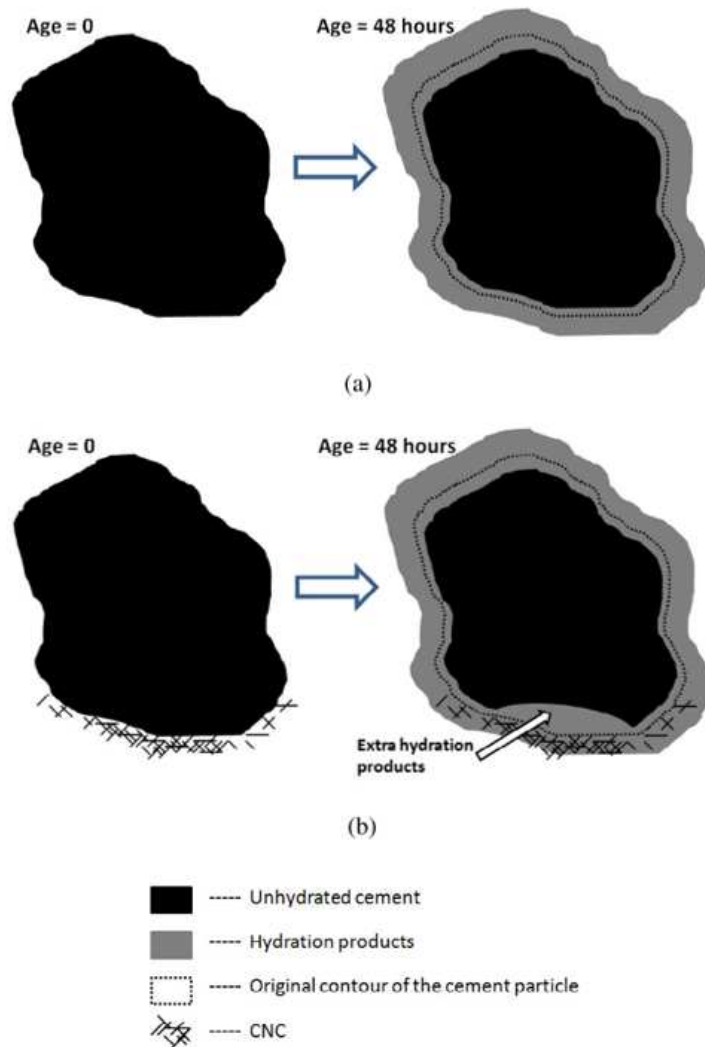
Source: Mejdoub et al. (2016).

In fact, Hisseine et al. (2020) observed that nanoscale cellulose filaments enhanced the degree of hydration of ultra-high performance concretes because the nanoadmixture increased the amount of chemically bound water and provided a supplementary source of water. The hydrophilic and hygroscopic features of NFCs enabled a time-dependent water release and contributed to replenish the empty matrix pores, decrease autogenous shrinkage, and reduce the risk of cracking at early ages. Bhalerao et al. (2015) also state that these nanoadmixture can improve the mechanical performance and fracture characteristics of cement-based composites by arresting micro-cracks formed during hydration and preventing their further growth.

Jiao et al. (2016) used a mercury intrusion porosimeter to verify that the porosity of cement pastes containing 0.00%, 0.15%, and 0.40% of NFC (by weight of cement) are 13.9%, 13.5% and 16.2%, indicating that the total amount of pores decreases with the incorporation of NFCs, reaching minimum at 0.15% NFC. The authors explain that NFCs release water during the curing process, providing the hydration of un-hydrated cement

particles and the formation of cement hydrates that reduce the porosity of the cementitious matrix.

Figure 11 - Illustration of the formation of hydration products around the cement particle from 0 to 48 hours in (a) pure cement paste and (b) cement paste with CNCs, based on the SCD mechanism.



Source: Cao et al. (2015).

Onuaguluchi, Panesar, and Sain (2014) also point out that hydration is intensified due to the alkaline hydrolysis of NFCs. The hydrolysis of cellulosic nanofibres leads to the formation of acidic and non-acidic organic products (Knill; Kennedy, 2003), an exothermic process that increases the heat evolution and favors the cement paste hydration.

Sun et al. (2016) reported that NFC characteristics, such as large surface area, high surface free energy, and the existence of many hydroxyl groups, contribute to the hydration and consequently improve the mechanical performance of cementitious

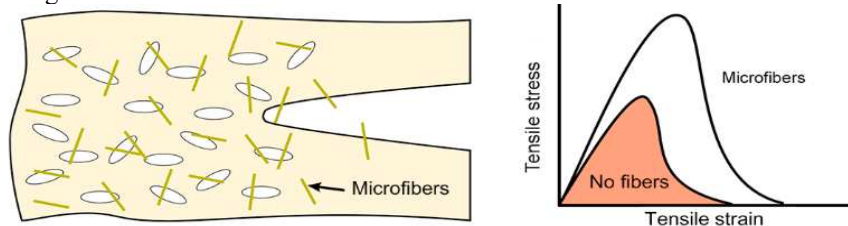
materials. The hydroxyl groups also act in the intimate interaction of cellulose with C-S-H and calcium hydroxide through hydrogen bonds (Hoyos; Vazquez, 2013). Dai et al. (2015) and Correia et al. (2018) also point out the contribution of hydroxyl groups to enhance the interaction between NFCs and the cement matrix.

Moreover, previous studies reported that NFCs can improve the matrix packing density, decrease the composite's porosity, and improve the mechanical properties of the interfacial transition zone (Hoyos et al., 2019; Sun et al., 2016).

Previous research also reported that the chemical effect of NFCs on the hydration process of cement pastes is small at early ages (e.g., 3 days) and much less significant than the effect of high water/cement ratios (higher than 0.50) on the cement hydration (Zhang; Scherer, 2020). For a water/cement ratio of 0.50, a study developed by Onuaguluchi et al. (2014) reported that NFCs delay the peak hydration time at early ages, as they reduce the rate of dissolution of the cement particles and the mobility of cement ions due to the viscosity of the nanofiber suspension. However, at 28 days there is a positive effect of nanoparticles on the hydration of the matrices (Onuaguluchi; Panesar; Sain, 2014).

Another mechanism that explains the increase in mechanical properties is the bridging effect, in which the fibers intercept the cracks in the matrix, preventing their propagation, increasing the fracture energy, and preventing a brittle failure (Correia et al., 2018; Dai et al., 2015; Fonseca et al., 2019; Peters et al., 2010). This effect is shown in Figure 12. It is noted that the graph is similar to that shown in Figure 5, corresponding to the results of Peters et al. (2010). The contributions of the bridging effect to enhance the mechanical properties of the composites seem to be also related to their age. At later ages, a better bond is established between NFCs and the cementitious matrix because the skeleton of the hydrated system is well structured, which enhances the adherence of the fibers into the hydrated system (Hisseine et al., 2020).

Figure 12 - Schematic of the fiber reinforcement mechanism in cementitious matrices.



Source: Fu et al. (2017).

One aspect that influences the effect of NFC in cementitious matrices is their concentration. In general, lower contents of nanofibrils increase the mechanical properties and higher quantities have the opposite effect. In large quantities, the NFCs present a non-homogeneous dispersion in the matrix. The agglomerations of fibers create pores that configure areas of weakness in the structural elements (Mejdoub et al., 2016; Onuaguluchi; Panesar; Sain, 2014; Sun et al., 2016). Hisseine et al. (2020) also reported adverse effects of high NFCs contents, such as the difficulty of ensuring adequate dispersion and air entrapment issues. Therefore, the content of admixtures and dispersion efficiency of NFCs in the cement matrices must be carefully considered.

2.3.4. Effects of NFC on the durability of cement-based composites

In order to access the durability of cement-based composites with NFCs, some studies in the literature performed tests of accelerated aging (Ardanuy; Claramunt; Toledo Filho, 2012; Claramunt et al., 2019; Correia et al., 2018), accelerated sulfate attack (Goncalves et al., 2019), and stiffness at higher temperatures (Hoyos et al., 2019).

Ardanuy, Claramunt, and Toledo Filho (2012) compared the effects of the dimensions of sisal fibers on the durability of mortar subjected to accelerated aging. Sisal pulp fibers with a diameter of 15.9 μm and NFC with diameters ranging between 25 and 250 nm were used. An NFC content of 4% (by weight of cement) was used in cement composites containing only NFCs as natural reinforcements. After 7 days of curing, the specimens were subjected to 5 wet-dry cycles. After these cycles, specimens containing NFCs presented an increase of 7% in their flexural strength, an increase of 15% in their flexural modulus, and a decrease of 15% in their fracture energy. On the other hand, control specimens without NFCs exhibited a decrease of 6% in their flexural strength, an increase of 44% in their flexural modulus, and a decrease of 15% in their fracture energy. Therefore, the authors concluded that NFCs did not provide significant improvements in the durability of the cement composites.

The durability of cement mortars containing combinations of different contents (0%, 2%, 4%, 6%, and 8% by mass of cement) of conventional pulps and nanofibrillated cellulose was also evaluated by Claramunt et al. (2015) through accelerated aging tests. Specimens containing higher contents of NFCs exhibited increases in flexural strength up to 16%, increases in modulus of elasticity up to 55%, and maintained their original fracture energy values after being subjected to 20 wet/dry accelerating aging cycles. On

the other hand, specimens containing higher contents of conventional pulps presented lower flexural strength and fracture energy values after aging. The authors concluded that NFCs were able to ensure increases of fiber-bonding due to aging effects and improve the densification of the interfacial zones.

Correia et al. (2018) performed an accelerated aging test of two groups of extruded cement-based composites: one of them containing 9% bamboo pulp (in relation to the total dry mass content) and the other with 8% bamboo pulp + 1% NFC. After 28 days of curing, the samples were subjected to 200 wet-dry cycles. Specimens containing 1.33% of NFC (by weight of cement) showed better mechanical performance after aging, with an increase of 20% in flexural strength, an increase of 25% in modulus of elasticity, and negligible changes in fracture energy and fracture toughness. Hence, degradation after accelerated aging of composites containing NFC was not observed.

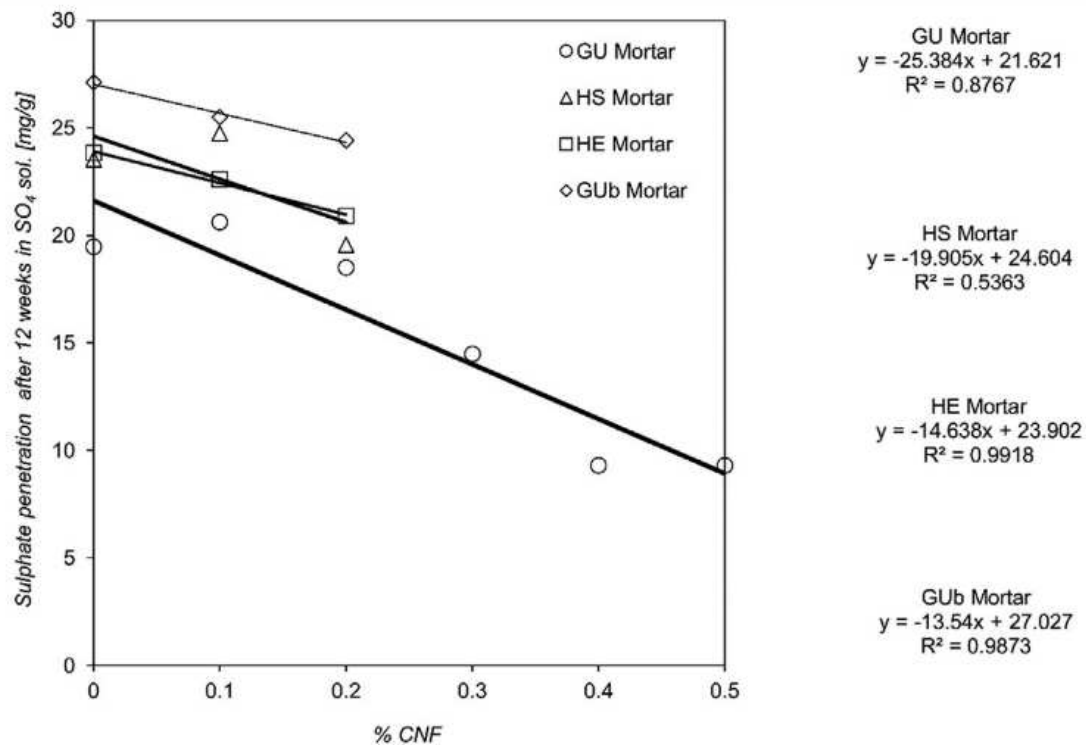
Claramunt et al. (2019) evaluated the effects of adding different NFC and CNC contents (ranging between 0.1% and 0.8% by weight of cement) in pastes cured at 20 °C and 60 °C for 28 days. After curing, they subjected some specimens to accelerated aging with 4 wet-dry cycles to intensify the degradation of nanocelluloses and evaluate the composites' durability. For calcium aluminate cement pastes, the addition of NFC does not contribute to preventing the increase in porosity of the matrix. In the ordinary Portland cement pastes, the samples with and without the addition of NFC showed similar behaviors.

Goncalves et al. (2019) conducted a pioneering study to evaluate the effect of adding NFC into pastes and mortars subjected to sulfate attacks. The binders used were: general use cement (GU); high-sulfate resistance cement (HS); high-early strength cement (HE); and a mixture of 70% GU and 30% fly ash (GU_b). Commercial cellulose nanofibrils with diameters ranging from 10 to 50 nm and length greater than 2 μm were added in the concentration of 0%, 0.26%, 0.52%, 0.77%, 1.03%, and 1.29% (by mass of cement) in cement mortars. For contents up to 0.26% of NFC, the reduction in sulfate penetration was small. However, the decrease was very significant (approximately 50%) for the addition of NFC contents of 1.03% and 1.29%, as shown in Figure 13. The authors also investigated the length changes of specimens immersed in a sulfate solution and observed that the presence of NFC decreased the expansion caused by sulfate attack.

Goncalves et al. (2019) attribute the lower penetration of sulfates to the hydroxyl groups of the NFC molecules and to the short circuit mechanism that intensifies the matrix's hydration, consequently reducing the porosity of the specimens. The smallest

dimensional variation is associated with the bridging effect promoted by nanofibrillated celluloses and the lower concentration of sulfates due to the greater refinement and lower permeability of the matrix.

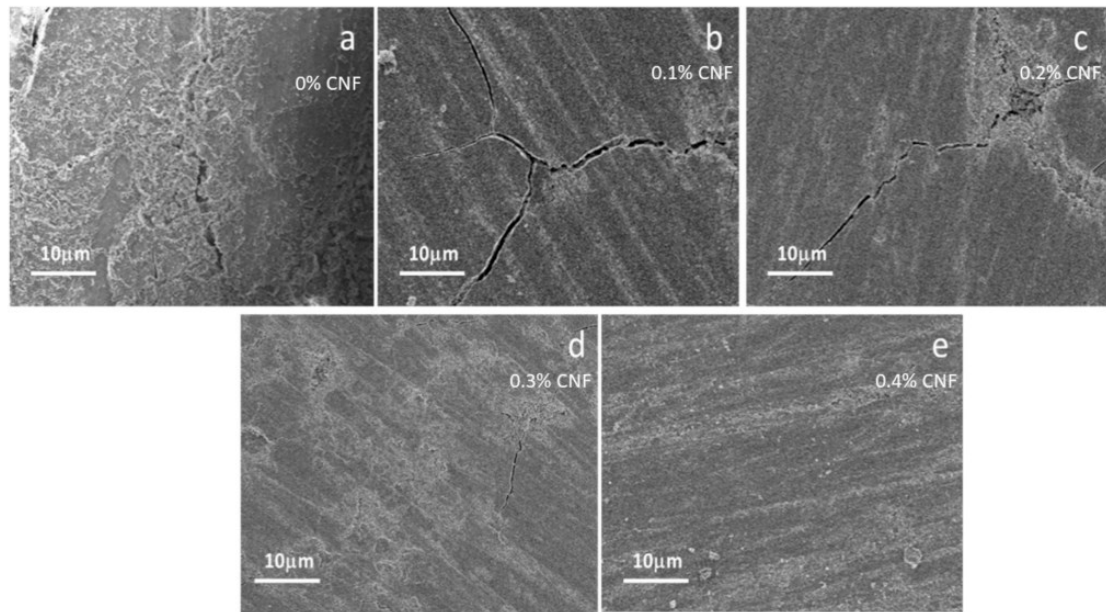
Figure 13 -: Sulfate penetration at 3 mm depth in different samples after 12 weeks of exposure.



Source: Goncalves et al. (2019).

Hoyos et al. (2019) undertook a dynamic thermo-mechanical analysis on cement pastes with NFC dosage of 0.1%, 0.2%, 0.3% and 0.4% (by mass of cement), varying the temperature from 35 to 250 °C. The storage modulus of the hardened pastes was measured to determine their elastic response (stiffness). They found that concentrations between 0.2 and 0.4% of NFC increased the storage modulus of the samples at 200 °C, which is associated with a better control of the microcracks generated by the expansion and evaporation of the water (Figure 14). In the temperature range from 25 °C to 200 °C, the highest storage modulus values were observed in composites containing 0.4% of NFC. They presented storage modulus up to 17% higher than that of control cement pastes.

Figure 14 - Field emission scanning electron microscopy of the cement paste surface with additions of (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.3% and (e) 0.4% NFC.



Source: Hoyos et al. (2019).

Research reviewed in the present section shows that some durability properties of cement matrices with NFC concentrations ranging between 0.10% and 8.00% (by weight of cement) had been evaluated. The lowest NFC concentration previously investigated was 0.1% (by mass of cement), which was found to be able to avoid mechanical degradation of flexural strength and elastic modulus due to accelerated aging. Similar results were observed for other small NFCs concentrations, such as 0.2%, 0.4%, and 0.8% (by mass of cement) (Claramunt et al., 2019). However, a comparison between the experimental results of other studies (Ardanuy; Claramunt; Toledo Filho, 2012; Claramunt; Ardanuy; Fernandez-Carrasco, 2015; Correia et al., 2018) suggests that increases in NFC concentration up to 8% (by mass of cement) caused the mechanical properties of cement-based composites (e.g., flexural strength, flexural modulus, modulus of elasticity) to increase after accelerated aging. Previous works (Goncalves et al., 2019; Hoyos et al., 2019) also reported that samples with the highest NFCs concentration presented the lowest sulfate penetration and highest thermal resistance. Therefore, the effects of high NFC contents on the durability of cement matrices seem to be different from the effects observed on their mechanical performance, since higher NFC dosage provided the highest increases in mechanical properties after aging, the highest decreases in sulfate penetration, and the highest increases in storage modulus for temperature levels up to 200 °C (Claramunt; Ardanuy; Fernandez-Carrasco, 2015; Goncalves et al., 2019; Hoyos et al., 2019).

The experimental works reported the best durability properties for the highest NFC concentrations investigated. For example, the highest increases in the mechanical properties due to aging effects were observed in composites containing 8% of NFCs (by mass of cement). The highest improvements in sulfate resistance were observed in composites containing 0.45% and 0.58% of NFCs (by mass of cement). The highest storage modulus at high temperatures were verified in cement matrices with 0.4% of NFCs (by mass of cement). This review indicated that the most significant mechanical improvements after accelerated aging provided by NFC were increases of 20% in flexural strength, 15% in flexural modulus, 55% in modulus of elasticity, in addition to the increases of 50% in sulfate resistance and 17% in storage modulus at high temperatures observed in cement composites containing NFCs, in relation to control specimens.

Studies of the effect of NFC on the durability of cementitious matrices are still scarce and quite recent. Most of the durability studies cited in this review article were published in 2019. The mechanisms behind the durability improvements are directly related to the different phenomena described in Section 2.3.2. Despite the limited data about this topic, it can be summarized that NFC can improve the resistance to aggressive agents as a result of increased refinement of the cement matrix, nucleation effects, bridging effects, and microcracks prevention. Thus, NFCs provide a cementitious matrix that is more compact and less permeable to aggressive agents, as Goncalves et al. (2019) suggested.

2.4. THE BEHAVIOR OF NFCs IN THE ALKALINE ENVIRONMENT OF THE CEMENT MATRIX

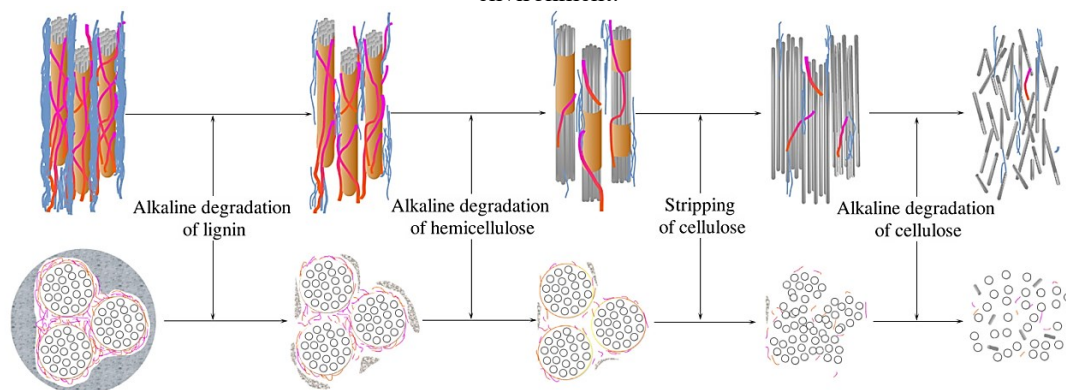
Previous studies have reported the degradation of vegetable fibers in inorganic matrices in the long-term due to the movement of alkaline pore water in and out of the fibers during wetting and drying cycles (Fu et al., 2017; Santos; Teixeira; Savastano Junior, 2017). This section summarises the main progress of existing research on the degradation of NFCs in the high-alkali environment of cement matrices.

Wei and Meyer (2015) studied the degradation mechanisms of natural cellulose fibers in alkaline and mineral-rich environments (inherent characteristics of cementitious matrices). For this purpose, they added a 2% volume fraction of sisal fiber in OPC pastes. They also evaluated the degradation of fibers when 10% and 30% of the cement mass was replaced by metakaolin. The authors describe that lignin and pectin are the first

components that degrade in the alkaline environment of pastes. Hemicellulose is also degraded, which decreases the integrity of the cell walls. Afterward, the degradation of the amorphous regions of the cellulose nanofibrils occurs, causing their interruption and consequent formation of CNC. The crystalline regions of the fibrils do not degrade because they are more stable. Figure 15 shows the fiber degradation process. As degradation occurs, cement hydration products, such as C-S-H and portlandite, infiltrate into the cell wall. This process is responsible for the mineralization and embrittlement of the fibers (Wei; Meyer, 2015).

The research carried out by Wei and Meyer (2015) also indicated that the replacement of 30% cement by metakaolin (in mass) effectively improved the durability of sisal fibers. It demonstrates that controlling the pH of the solution in the matrix pores is an efficient way to mitigate the degradation of natural fibers.

Figure 15 - Diagrammatic sketch of the degradation process of natural fibers in an alkaline environment.



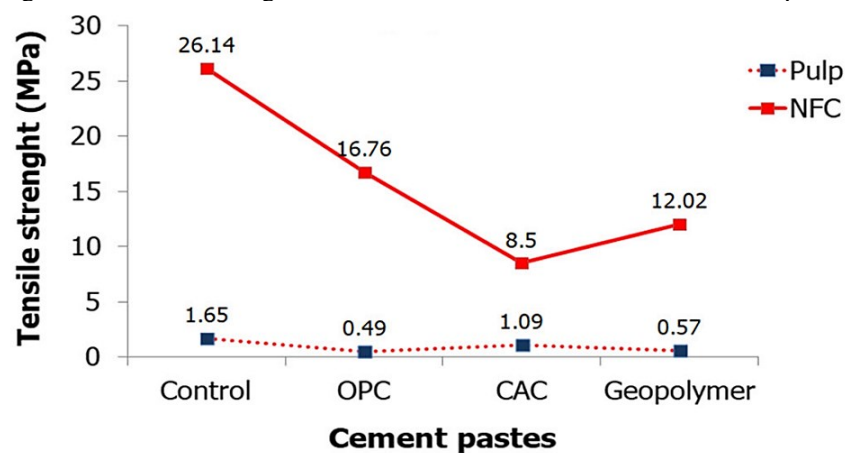
Source: Wei; Meyer (2015).

Correia et al. (2019) also studied the degradation of cellulose fibers (bamboo pulp and NFC) in OPC, CAC, and geopolymers (GP). In the case of pulps, there was a reduction in the tensile strength of the fiber sheets by 70%, 34%, and 65% after immersion in OPC, CAC, and GP, respectively. The tensile strength of NFCs was also reduced, with decreases of 36%, 67%, and 54% after immersion in OPC, CAC, and GP, respectively (Figure 16). The reductions were attributed to the chemical modifications of lignin, cellulose, and hemicellulose on the fiber surfaces due to the pastes' high alkalinity.

Correia, Santos, and Savastano Jr. (2015) evaluated two groups of cellulose fiber-cement composites: one with the addition of 9% eucalyptus pulp (in relation to the total dry mass content) and the other with 8% eucalyptus pulp + 1% NFC. After two days of curing in a saturated air condition, the samples were subjected to accelerated supercritical

carbonation and then mechanically tested. Carbonation increased the flexural strength and decreased the porosity of the mixtures since it reduces fiber degradation by lowering the pH and leads to matrix densification through the precipitation of calcium carbonate in the pores. Santos et al. (2015) and Urrea-Ceferino et al. (2017) also obtained lower degradation of cellulose pulp fibers in cementitious matrices when applying a supercritical carbonation treatment in the early ages of the specimens.

Figure 16 - Tensile strength of fibers after immersion in different cement pastes.



Source: Correia et al. (2019).

These studies demonstrate that the alkaline environment of cementitious matrices is not ideal for the structure of cellulose fibers and nanofibers, generating their degradation and loss of strength. This limitation can be circumvented by using materials that lower the pH of the matrix (Correia et al., 2019) or by accelerated carbonation (Correia; Santos; Savastano Júnior, 2015; Santos et al., 2015; Urrea-Ceferino et al., 2017). However, the various works mentioned in the previous topics prove that even in conventional mixtures with high pH and the degradation of fibers, NFCs can promote gains in the mechanical properties, refining the cement matrix, and increasing the durability of cementitious composites.

2.5. CONCLUSIONS AND RESEARCH PROSPECTS

The manuscript presents a critical overview of the recent progress of mechanical and durability properties of cementitious materials reinforced with NFC. It filled an existing gap in the literature since previous papers have reported more general reviews,

dealing with various nanocellulose types, such as NFC, bacterial nanocellulose, and cellulose nanocrystals.

This systematic review highlighted that NFCs have characteristics that make them attractive in different areas. In civil construction, they have shown improvements in cementitious matrices since they increase the hydration of pastes, compressive and flexural strengths, and stiffness of the cement-based composites. They also collaborate to increase fracture energy and decrease microcracks by bridging effect. Finally, they make the matrix more cohesive and less porous, playing an important role in decreasing the penetration of sulfates and with great potential in increasing the durability of concrete structures.

NFC has great environmental appeal because it is a biodegradable, renewable, and non-petroleum-based material. These characteristics are important for civil construction since the sector consumes large amounts of natural resources and emits high amounts of CO₂. Therefore, the use of NFC in cementitious matrices can collaborate to make construction products more sustainable.

Although the use of NFC in cementitious matrices is promising, some topics require attention. For instance, further studies are recommended to optimize the production and pre-treatment processes of NFC, in order to increase the mechanical strength and stiffness benefits provided by these nanoadmixture. Research is also needed to improve the ductility of cement-based composites containing NFC, while keeping these mechanical strength and stiffness benefits.

Most research has focused on the mechanical performance of cement structures, with few studies addressing their durability. Thus, more in-depth studies focused on the durability of NFC in the alkaline environment of cement matrices and the implication of their degradation on the performance of concrete structures are necessary. Another point to be investigated in future works is the development of techniques that minimize the degradation of fibers and that can be applied in real, common, and large structures.

Systematic experimental investigations of the resistance of NFC-based composites to aggressive agents, water permeability, and freeze-thaw damage are also strongly recommended since they were not carried out in the previous works. Although high NFC contents were found to increase different durability properties of cement-based composites, the previous studies did not report an optimal NFC dosage, in terms of durability improvements. In most of the cases, the best durability properties were observed in composites containing the maximum nanoreinforcement concentration, so

that higher durability improvements could be observed if higher NFC concentrations had been used. Further analysis is also recommended to detect if an excessive dosage of NFC would have adverse effects on some durability properties. In addition, contents that optimize the mechanical properties were found to be different from those that usually provide the best durability results. Therefore, future studies are needed to identify the most recommended NFC dosage, in terms of ensuring the highest mechanical and durability benefits.

Since the agglomeration of NFCs can generate weak zones in the structural elements, practical efforts are needed to develop techniques for dispersing nanocellulose fibers during the production of concrete. Such techniques should preferably demand low energy consumption and be able to disperse the fibers in large volumes of material. Hence, future research is needed to develop simplified and efficient dispersion methods that allow a large-scale application of NFCs in the construction sector. The effects of different NFC dispersion methods on both mechanical and durability properties of cement composites are also required in future research.

In addition, there is no previous assessment of the life cycle impacts of the production of NFC-based concretes. Then, a detailed life cycle assessment of cement-based materials containing NFCs is strongly recommended to update the information regarding their environmental performance.

Another concern about the incorporation of nanocelluloses in cement-based composites is the cost-competitiveness with the traditional technology of plain cement-based composites. However, the recent and fast technological development has provided the manufacture of nanocelluloses with relatively low cost. Therefore, once durability, dispersion, and cost-competitiveness issues are overcome, the use of NFC for sustainable civil construction will become profitable and will have a large expansion field.

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CHAPTER 3²: INFLUENCE OF NFC SONICATION TIME ON THE PERFORMANCE OF CEMENTITIOUS COMPOSITES CONTAINING STEEL SLAG

Abstract: *Incorporating waste into cement composites for civil construction is seen as a promising and necessary practice, addressing improper waste disposal and reducing the extraction of natural resources. Nanomaterials are utilized to enhance the mechanical properties of these composites, offering potential improvements to waste-based materials and minimizing potential drawbacks. This study combines these strategies by using basic oxygen furnace slag (BOFS) as an aggregate and unbleached nanofibrillated cellulose (NFC) as a nanomaterial, creating an eco-efficient cement composite. The assessment involves studying the dispersion and stability of aqueous NFC solutions with different sonication times, evaluating workability, compressive strength, flexural strength, and overall eco-efficiency of the specimens. Results indicate improved NFC dispersion and stability through sonication, leading to enhanced mechanical performance and eco-efficiency. However, excessively long sonication times negatively impact these outcomes. In conclusion, sonication is an efficient technique for superior cement-based composites with BOFS and NFC, emphasizing the importance of optimal sonication duration.*

Keywords: Dispersion of nanomaterials, nanofibrillated celluloses, steel slag, cement-based composites, mechanical performance, eco-efficiency.

3.1. INTRODUCTION

In recent times, there has been a growing pursuit of sustainable alternatives for various services and products. This trend has a notable effect on industries that exert significant pressure on the environment. Construction, in particular, stands out as a major consumer of natural resources such as rocks, metals, wood, and water, among others. It is also a substantial energy consumer, a significant producer of waste, and a major contributor to greenhouse gas emissions (Li et al., 2022; Sev, 2009).

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To mitigate environmental impacts and decrease the extraction of natural resources, it is possible to substitute cement composite aggregates with waste materials. Numerous studies have demonstrated the viability of utilizing demolition waste for this purpose (Abera, 2022; Cantero et al., 2022; Wu et al., 2021), mining (Benahsina et al., 2022; El Machi et al., 2021; González et al., 2020), agricultural solid (Khankhaje et al., 2016; Liu; Li; Ni, 2022; Shao; Du; Zhou, 2021) and metallurgy (Franco de Carvalho et al., 2019a, 2020; Mirnezami; Hassani; Bayat, 2023) wastes. In this final category, it is important to highlight basic oxygen furnace slag (BOFS), which originates from steel production utilizing the Linz-Donawitz process. This byproduct is generated on a large scale by industry (Fernández-González et al., 2019; Worldsteel Association, 2021), and primarily consists of four oxides: lime (CaO), periclase (MgO), silica (SiO₂), and wustite (FeO) (Yildirim; Prezzi, 2011). Utilizing waste as aggregates offers the advantage of diminishing the extraction of rocks and sand from natural sources while offering a suitable disposal solution for materials no longer in use by industry. Additionally, BOFS presents other advantages, including strength comparable to or even surpassing that of conventional aggregates (Geiseler, 1996) and greater rugosity, maximizing interaction with the matrix (Qasrawi, 2014).

Various methods can be employed together to strengthen and increase the durability of the produced materials. The potential for improved strength also implies the opportunity to use less cement, and incorporating more durable materials reduces the need for frequent interventions and replacements. Currently, the use of nanomaterials to improve the performance of cementitious materials has been highlighted (Onaizi et al., 2021; Yoo; Oh; Banthia, 2022). Studies incorporating various nanoparticles such as carbon black (Dehghanpour; Yilmaz; Ipek, 2019; Wang et al., 2022), carbon nanotubes (Gao et al., 2020; Hassan; Elkady; Shaaban, 2019), TiO₂ (Pathak; Vesmawala, 2022; Ren; Lai; Gao, 2018), and others can be found in the literature. One noteworthy nanoparticle is nanofibrillated cellulose (NFC), an organic and renewable material capable of significantly enhancing the mechanical strength and durability of cement pastes, mortars, and concretes (Santos et al., 2021). These improvements are attributed to several mechanisms. NFCs can serve as nucleation points for hydrated crystals during the early stages of cementitious material (Mejdoub et al., 2016). The hydroxyl groups on the fiber surface also interact with the hydrated cement products, enhancing the matrix interaction (Hoyos; Vazquez, 2013). Interestingly, the interaction of NFCs with the cement grain surpasses the interaction between cement particles, which, in turn, is greater than the

interaction between fibers. (Zhong et al., 2022). In addition, Cao et al. (Cao et al., 2015) proposed a short-circuit diffusion (SCD) mechanism, where fibers surround the cement particle, forming channels that facilitate water entry, promoting the hydration of cement particles. Lastly, NFCs play a role in connecting cracks in the matrix through a bridging effect, preventing crack propagation and enhancing matrix strength while preventing brittle ruptures (Peters et al., 2010).

Nevertheless, for fibers to effectively impact the cement matrix through various mechanisms and optimize the product's performance, they must be well-dispersed (Nassiri et al., 2021; Santos et al., 2021). Achieving better dispersion of NFCs involves using surfactants or stabilizing agents, pre-treating fibers (e.g., TEMPO Mediated Oxidation Pre-Treatment), employing magnetic or mechanical stirring, and utilizing sonication (Oliveira de Souza et al., 2022). The latter technique relies on the principle of cavitation, where ultrasonic waves applied by sonicators induce the formation of bubbles in low-pressure wave regions. The collapse of these bubbles generates a significant shear force, facilitating the dispersion of fibers (Noltingk; Neppiras, 1950). Sonication has proven successful in achieving NFC dispersion in some studies (Jiao et al., 2016; Mejdoub et al., 2016; Nassiri et al., 2021; Onuaguluchi; Panesar; Sain, 2014).

Previous studies have not assessed the optimization of NFC dispersion in eco-efficient cementitious matrices incorporating BOFS. Determining an optimal sonication energy is challenging, mainly because previous research on this topic is scattered and concentrated on conventional cementitious matrices without incorporation of waste materials. There has been no previous investigation into the impact of varying sonication energy levels on the mechanical properties of eco-efficient mortars made with BOF and NFCs. Consequently, any potential synergistic effects between BOFS and NFCs regarding dispersion enhancements in cementitious matrices remain unknown. In this sense, the present study aims to investigate how the dispersion time of nanofibrillated cellulose influences the mechanical strength of a cementitious composite incorporating steel slag aggregates. To accomplish this, diverse techniques and tests are applied.

3.2. MATERIAL AND METHODS

3.2.1. Materials

The conventional binder used to produce the specimens investigated in this research was CPV-ARI cement, corresponding to ASTM type III. This particular cement features a low mineral admixtures content (ABNT, 2018), minimizing interactions of other additions with the residues and nanomaterials investigated. The specific gravity of the cement was measured at 3.05 g/cm^3 according to the ABNT NBR 16605 standard (ABNT, 2017).

The fine aggregates were BOFS provided by the Arcelor-Mittal Company and previously stored for five years in the Laboratory of Civil Construction Materials patio at the Federal University of Ouro Preto - UFOP, State of Minas Gerais, Brazil. Throughout this storage period, the residue underwent a weathering process aimed at stabilizing the expansive oxides. The initial BOFS had a gray color, particle size ranging between 6.35 and 12.5 mm, and a specific gravity of 3.57 g/cm^3 , as characterized by Martins et al. (Martins et al., 2022).

A polycarboxylate-based superplasticizer (MC-PowerFlow 4001) was employed as an additive to enhance the workability of the mixture and decrease the water/cement ratio in the cementitious composites.

The unbleached NFC from Pinus was produced and provided by Embrapa Florestas, situated in Colombo, state of Paraná, Brazil.

3.2.2. Production of NFCs

Initially, a suspension of non-bleached kraft pulp of loblolly pine (2%, w/v) was prepared using distillate water, and then it was fragmented using a 450 W blender for 10 min. Subsequently, it was subjected to further grinding using a supermasscolloider Masuko Sangyo Microfluidizer (Masuko Sangyo Ltd., Kawaguchi, Japan). The equipment operated at 1500 rpm and a distance between discs of 0.1 mm. The cellulose pulp was reloaded 30 times through the friction between the silicon carbide ceramic disks; the abrasive forces induced defibrillation on the cellulose. During this process, the fibers were reduced to nanometric sizes (0.1 and 100 nm), and with this procedure, it was possible to obtain a nanosuspension formulation that exhibits gel-like characteristics.

3.2.3. Characterization of NFCs

The solids content of the NFC gel was determined by the mass difference between the samples in their natural state and those dried at 100-105 °C for up to 24 hours. The specific gravity of the gel was assessed using a 10 ml volumetric flask (Figure 1). Utilizing the values of specific gravity and solids content of the gel, along with the density of water, the specific gravity of the nanofibers was calculated. Table 1 presents the main results.

Figure 1 - Volumetric flasks for determination of specific gravity.



Source: The author (2024).

Table 1 - Properties of the NFC used in the research.

Property	Result
Gel concentration (%)	1.08
Gel specific gravity (g/cm ³)	≅ 1
NFC specific gravity (g/cm ³)	1.08

Source: The author (2024).

3.2.4. UV-vis

The Ultraviolet-visible (UV-vis) spectroscopy technique was employed to examine how the sonication time affects the dispersion of NFCs in aqueous solutions. To do this, 12.5 ml samples were produced with a concentration of 0.02% NFC relative to the mass of water. These samples underwent various sonication times: 0, 0.04, 0.08, 0.16, and 0.32 min/ml of solution.

Following preparation and sonication, UV-vis analyses were carried out in the FluoroMax Plus fluorometer. The UV-vis lamp was set at a selected wavelength of 300

nm (Parveen et al., 2017, 2018), and absorption readings were taken within the range of wavelengths from 200 to 800 nm.

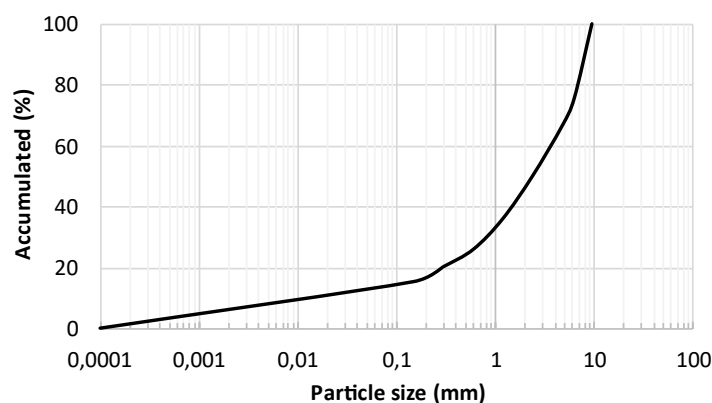
3.2.5. Zeta potential

The zeta potential values of NFC solutions were measured by a Zeta Sizer NanoSeries equipment. Samples were prepared as described in section 3.2.4. Three readings were taken from each sample, and the average value was adopted.

3.2.6. Preparation of the BOFS aggregate

To obtain the fine aggregate, the BOFS was initially dried in an oven for 24 hours. Subsequently, the residue underwent processing in a "Los Angeles" machine (equipment standardized by ABNT NBR 16974 (ABNT, 2021) for 40 minutes. The particle size curve of the processed material is presented in Figure 2.

Figure 2 - Particle size curve of the BOFS aggregate produced with 40 min of grinding.



Source: The author (2024).

The resulting material was sieved, and the fraction with a diameter smaller than or equal to 2.36 mm was used as BOFS fine aggregate.

3.2.7. Packing factor evaluation and production of mortars

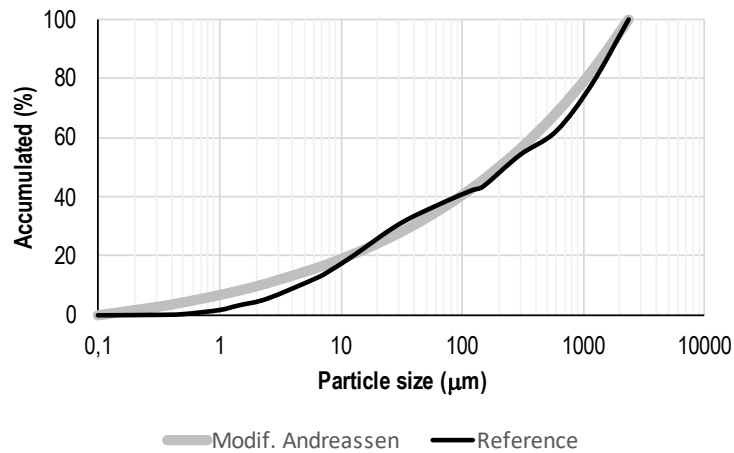
The modified Andreassen particle size distribution method (Funk; Dinger, 1994) was employed to ensure a tightly-packed reference mixture with reliable mechanical

properties. The curve was derived following Eq. (1), in which $CPFT$ represents the cumulative volume of particles with a size smaller than D , D_L is the diameter of the largest particle, D_S is the diameter of the smallest particle, and q is the distribution coefficient.

$$CPFT(\%) = 100 \frac{D^q - D_S^q}{D_L^q - D_S^q} \quad (1)$$

Distribution coefficient q , as reported in the literature, range from 0.21 to 0.37, with values between 0.25 and 0.30 commonly applied for high-performance and conventional concrete (Snehal; Das, 2021). In this study, a q value of 0.25 was chosen. Additionally, a D_L of 2.36 mm (representing the largest diameter of the fine slag aggregate produced) and a D_S of 0.0001 mm were adopted. The modified Andreassen curve determined that the most optimal mixture comprised 20% cement and 80% BOFS sand, following a 1:4 volume ratio. Figure 3 shows the curve corresponding to the reference mixture.

Figure 3 - Particle size distribution of the mixture 1:4 and modified Andreassen curve for $D_L = 2360 \mu\text{m}$, $D_S = 0.1 \mu\text{m}$ and $q = 0.25$.



Source: The author (2024).

3.2.8. Preparation of the cementitious composites

To assess the impact of fiber dispersion, cementitious composites were produced with a cement-to-fine aggregate ratio by volume of 1:4 and a NFC content of 0.01% in relation to the cement mass. To enhance workability, 2.80% of superplasticizer (SP) was utilized relative to the cement mass. The ratio between the volume of dry material and the

final volume of the mixture was 0.72, resulting in a water-to-cement ratio of approximately 0.63.

In the initial phase, an aqueous NFC solution was prepared. The specified amounts of water and NFC for mixing underwent sonication at various durations: 0, 0.04, 0.16, and 0.32 minutes per milliliter of solution, using a 50 W, 20 kHz probe sonicator. In parallel, BOFS sand and cement were dry mixed. Subsequently, the superplasticizer and the blend of sand and cement were introduced into the NFC solution. The addition and mixing of SP, sand, and cement took 10 minutes, followed by an additional 5 minutes of stirring for the complete mixture. The resulting mixture was poured into acrylic molds measuring 2 cm x 2 cm x 8 cm, in two layers. Each layer was compacted on a vibrating table for 15 seconds. After molding, the specimens were cured inside a moist room (23 ± 2 °C and 95% humidity). Additionally, cylindrical specimens measuring 3 cm in diameter and 6 cm in height were molded for future microstructural tests.

3.2.9. Workability measurement

Before molding the specimens, the mixture's workability was assessed using a mini-cone-slump test. The cone, with dimensions of 57 mm in height, 19 mm at the top diameter, and 38 mm at the bottom diameter (Kantro, 1980), was employed. Three layers of the mixture were added to the cone, with the first layer compacted with 15 strokes, the second layer with ten strokes, and the third layer with five strokes, aimed at removing air bubbles. Subsequently, the mold was lifted carefully, and ten drops from the flow table were applied, according to Kantro (Kantro, 1980). Finally, three values of spreading diameters were measured, and the average was adopted as the flow diameter.

3.2.10. Microstructural tests

After a curing period of 28 days, small slices from the intermediate portion of the cylindrical specimens were extracted, interrupting their hydration process with isopropyl alcohol, following the methodology outlined by Scrivener et al. (Scrivener; Snellings; Lothenbach, 2018). This material was subsequently utilized in various microstructural studies.

An X-ray diffraction (XRD) analysis was conducted, using the D8Discover diffractometer situated in the Department of Physics at the Federal University of Viçosa

(UFV). The radiation source employed was $\text{CuK}\alpha$, with a wavelength (λ) of 1.5418 Å, and the scanning range (2θ) ranged from 10° to 80°, with a 0.05° step size and an accumulated time per step of 1 s.

Scanning electron microscopy (SEM) images of NFC solutions with sonication times of 0, 0.04, 0.08, 0.016, and 0.32 min/ml were captured using a JEOL JSM-6010LA microscope at 15 kV, located in the Department of Physics/UFV. And SEM images of cementitious composites were captured at the Center for Microscopy and Microanalysis/UFV, utilizing the Leo 1430 VP Scanning Electron Microscope operating at 15 kV.

3.2.11. Evaluation of the mechanical performance of composites

The specimens, manufactured as outlined in section 3.2.8 underwent assessment at the 28-day mark for both compressive and flexural strength (ABNT, 2005; ASTM 2014, 2018). Additionally, the eco-efficiency of the mixtures was gauged following the methodology of Damineli et al. (Damineli et al., 2010; Damineli; Pileggi; John, 2013). Eco-efficiency was delineated by two parameters: cement intensity for compressive strength - CI_c (Eq. (2)), and cement intensity for flexural strength - CI_f (Eq. (3)).

$$CI_c = \frac{c}{p_c} \quad (2)$$

$$CI_f = \frac{c}{p_f} \quad (3)$$

The eco-efficiency of the mixtures is indicated by the values of CI_c and CI_f . Lower values for these parameters signify higher eco-efficiency. Specifically, they represent the amount of cement required to attain 1 MPa of compressive and flexural strength at 28 days, respectively.

3.3. RESULTS AND DISCUSSION

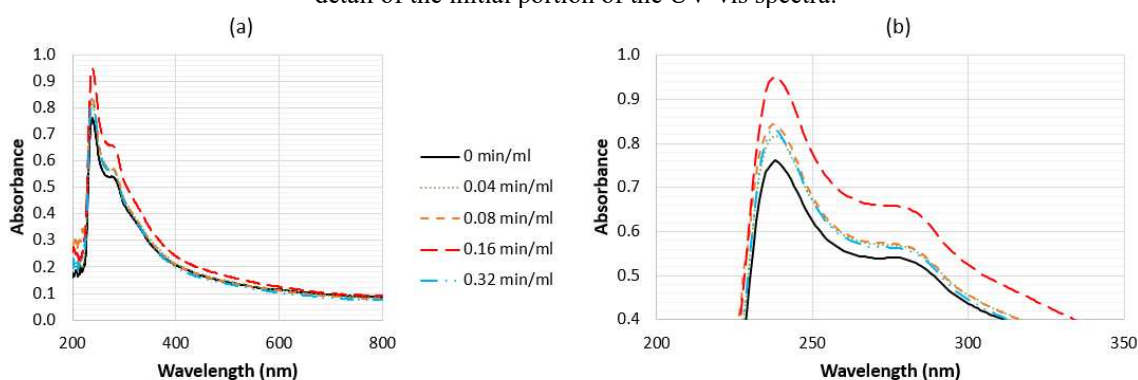
3.3.1. UV-vis

UV-vis spectroscopy is a technique that measures the absorption of light by samples as a function of wavelength. Light interacts with the material when passing

through the sample, causing electronic transitions. Such interaction is described by the Beer-Lambert law, which relates the fraction of light incident on the sample (I_0) and the fraction of light measured after interaction with the material (I) (Chen et al., 2013). A higher concentration of particles in solution will interact more with light, making UV-vis a suitable technique for measuring nanocellulose dispersion.

Figure 4 illustrates absorbance curves for various sonication times of aqueous NFC solutions. The unsounded sample displayed the lowest absorbance curve, while increasing sonication time correlated with higher absorbance up to 0.16 min/ml. However, longer sonication times promoted a drop in absorbance. These results align with those obtained by Parveen et al. (2017, 2018), who evaluated microcrystalline cellulose solutions prepared under different sonication times. It was found that with a short sonication time, there were larger cellulose agglomerates that tended to sediment, causing lower absorbance values. Up to 30 min of dispersion, sonication efficiently reduced the size of the agglomerates, with a consequent decrease in sedimentation and higher absorbance values. However, longer times promoted reagglomeration of the nanocellulose, reducing the absorbance of the samples. Therefore, the unbleached NFC evaluated in this work appears to have a similar behavior to the material evaluated by Parveen et al. (2017, 2018). And in fact, carbon nanotubes (CNT), materials that also have a high length/area ratio, exhibit the same behavior under sonication, with improved dispersion up to intermediate sonication times and reagglomeration at longer times due to the increase in energy and temperature (Dumée et al., 2013).

Figure 4 - Absorbance of solutions with different sonication times. In (a) general UV-vis spectra; in (b) detail of the initial portion of the UV-vis spectra.



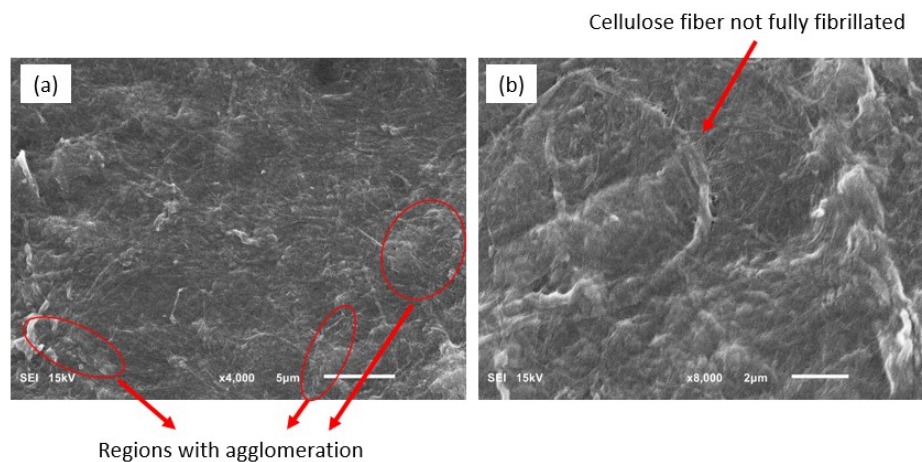
Source: The author (2024).

SEM images help explain the results. In samples that were not sonicated, some regions with a specific agglomeration of fibers were observed (Figure 5a). This suggests

inadequate distribution of NFCs, potentially hindering the enhancement of mechanical properties in the produced cementitious composites. Poor distribution could lead to weak points in the matrix (Mejdoub et al., 2016; SUN et al., 2016) and limit the efficiency of fiber-induced bridging effects. Additionally, Figure 5b highlights some fibers that are not fully fibrillated, indicating potential for optimization in the production of NFCs.

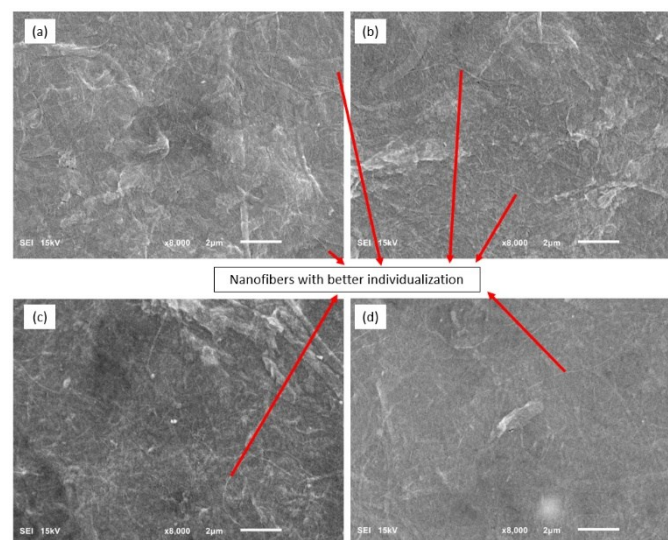
In Figure 6, longer fibers exhibiting better individualization are evident, indicating more efficient dispersion attributed to sonication. Therefore, this better dispersion prevents the formation of points of weakness in the matrix, maximizes the interaction between the fibers and the matrix, and prevents the proliferation of cracks during loadings of the cementitious composite.

Figure 5 - NFC samples without sonication: (a) 4000x magnification, (b) 8000x magnification.



Source: The author (2024).

Figure 6 - NFC samples with time sonication of (a) 0.04 min/ml, (b) 0.08 min/ml, (c) 0.16 min/ml and (d) 0.32 min/ml. 8000x magnification.



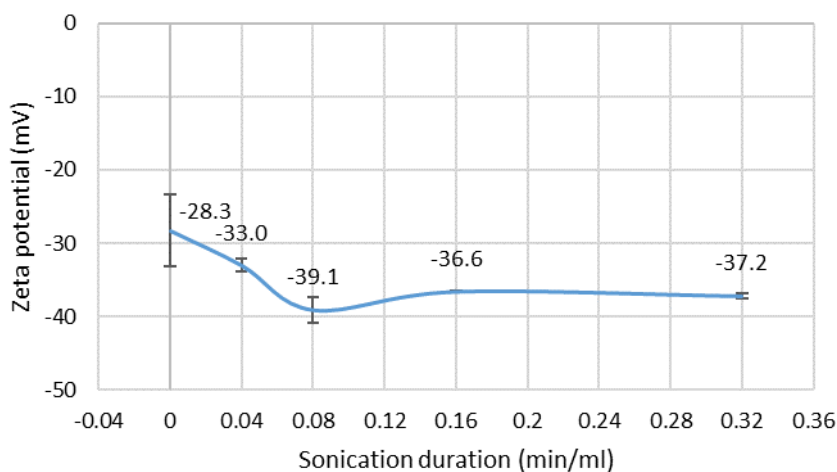
Source: The author (2024).

3.3.2. Zeta potential

The colloidal stability of cellulose nanomaterials is typically maintained through the repulsion of charged groups on their surface. The zeta potential technique, which measures the surface charge density of suspended particles, is commonly employed to assess the stability of suspensions (Foster et al., 2018).

Figure 7 displays the zeta potential values for samples subjected to different sonication times. Notably, the absence of sonication results in the least negative charge (-28.3 mV) with a broad dispersion of values. Upon sonication, the charge becomes progressively more negative, reaching -39.1 mV at 0.08 min/ml, and then stabilizes around -37 mV. Higher zeta potential values indicate improved stability of nanofibers, with suspensions falling within ± 10 to ± 30 mV considered slightly unstable and ± 30 to ± 40 mV as moderately stable (Sharma; Mandal; Goswami, 2021). Therefore, sonication emerges as an effective method for enhancing suspension stability. In conjunction with sonication, other techniques such as surfactants, stabilizing agents, or fiber pretreatment methods like TEMPO-mediated oxidation (Oliveira de Souza et al., 2022) could be explored to enhance particle charge.

Figure 7 - Variation of zeta potential values as a function of sonication duration.



Source: The author (2024).

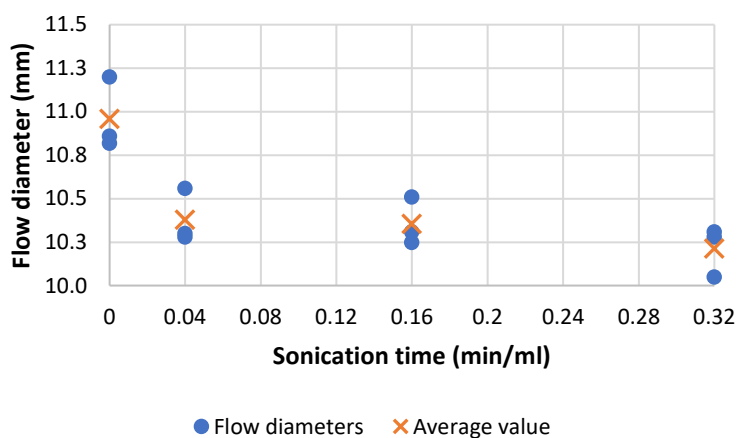
3.3.3. Workability

The flow diameters of the different mortars produced are shown in Figure 7. It is evident that the sample without sonicated NFCs exhibited the largest flow diameters. In

contrast, the other treatments resulted in smaller flow diameters. This difference can be attributed to the hydrophilic nature of the nanofibers (Nassiri et al., 2021). Improved fiber dispersion increases the surface area of NFCs, enhancing water retention and consequently reducing water availability in the system. As a result, the workability of the samples decreases. These findings align with the UV-vis results, indicating that sonication promotes more effective fiber dispersion.

To achieve higher amounts of added NFCs or improved fiber dispersion, it is advisable to adjust the superplasticizer dosage carefully. This adjustment aims to prevent any adverse effects on the compaction and molding of the specimens (Santos et al., 2021).

Figure 7 - Flow diameters of samples as a function of sonication time.



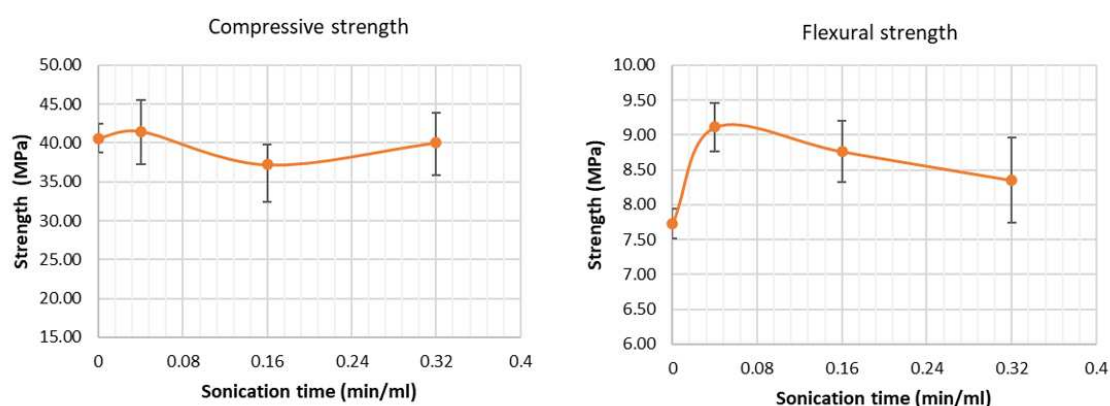
Source: The author (2024).

3.3.4. Mechanical performance

Regarding the compressive strength of the specimens at 28 days, the sonication treatment did not show statistical significance. In other words, longer sonication times do not necessarily lead to greater compressive strength (Figure 9 and Table 2). However, for flexural strength, it is evident that longer sonication times contribute to significant improvements. There is an increase of 17.9% and 13.4% for sonication times of 0.04 min/ml and 0.16 min/ml, respectively (Figure 9 and Table 3). With a sonication time of 0.32 min/ml, the strength gain in comparison to the reference is lower (8.1%). These results align with those observed in UV-vis and potential zeta technique, where fiber dispersion and stability are less effective without sonication. Although the flexural strengths are statistically equal between the sonicated samples, a tendency towards optimum strength is observed for intermediate sonication times.

Comparing the results, it is clear that the UV-vis technique effectively differentiates the non-sonicated sample from the sonicated ones. On the other hand, among the sonicated samples, the one sonicated for a time of 0.16 min/ml showed a higher absorbance than the others, which would indicate a more adequate dispersion in relation to the others. However, in the other techniques used, this sonication time did not have the best results. Therefore, a more in-depth study of the application of this technique in evaluating the dispersion of NFCs is recommended in order to make it more reliable in correlating sonication time, fiber dispersion, and read absorbance.

Figure 9 - Mechanical strength in relation to sonication time.



Source: The author (2024).

Table 2 - Tukey test for the compressive strength of mixtures at 28 days.

Sonication time (min/ml)	N	Mean	Grouping
0.04	8	41,42	A
0	7	40,616	A
0.32	8	40,00	A
0.16	8	37,22	A

Source: The author (2024).

Table 3 - Tukey test for the flexural strength of mixtures at 28 days.

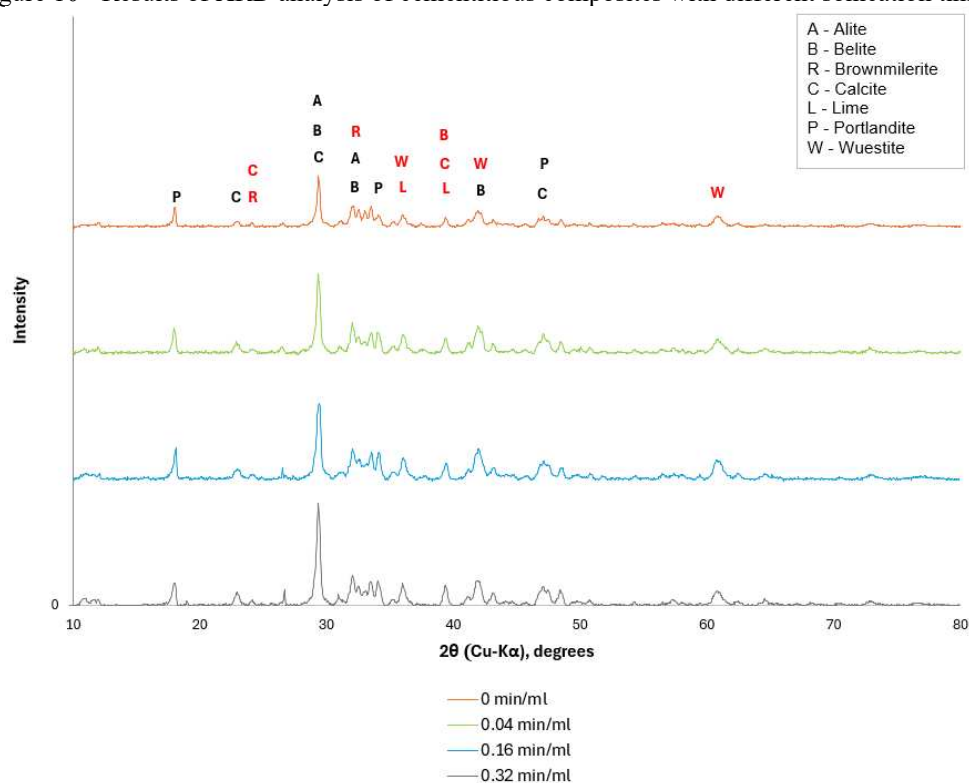
Sonication time (min/ml)	N	Mean	Grouping
0.04	4	9,115	A
0.16	4	8,766	A
0.32	4	8,355	A B
0	3	7,729	B

Source: The author (2024).

Within the cement matrix, NFCs contribute to mechanical strength through various mechanisms. Serving as nucleation points, they provide water to cement particles

and utilize a bridging effect to impede crack propagation (Balea et al., 2019; Cao et al., 2015). In the examined samples, the most influential mechanism was the bridging effect, leading to notable improvements in flexural strength. This conclusion finds support in XRD results, where curves for different sonication times exhibit similarity (Figure 10), suggesting no significant variations in mineralogical composition justifying increased strength with improved sonication. Furthermore, SEM images reinforce these findings. Samples without sonication exhibit suboptimal fiber distribution (Figure 11a) with noticeable agglomeration points (Figure 11b). In contrast, samples with higher flexural strength display improved fiber distribution (Figure 12a), and the presence of fibers contributing to the bridging effect (Figure 12b). Therefore, it can be inferred that sonication enhances the distribution of fibers into the matrix, optimizing the bridging effect.

Figure 10 - Results of XRD analysis of cementitious composites with different sonication times.

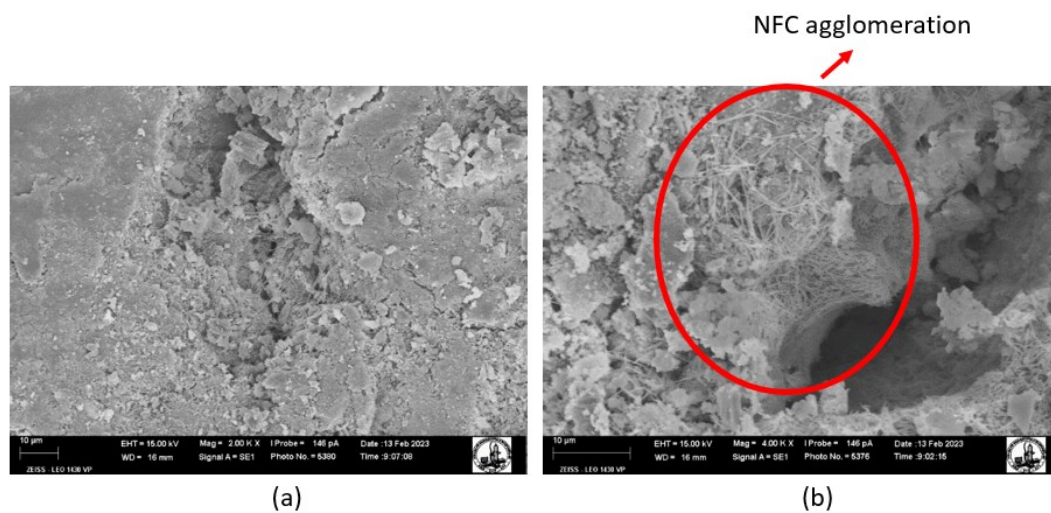


Source: The author (2024).

Figure 10 shows the XRD of the samples, where the black letters indicate compounds originating from cement and the red letters compounds from slag. Peaks of portlandite $[\text{Ca}(\text{OH})_2]$ were identified, derived from the hydration of alite (C_3S) and belite (C_2S) present in cement. C_3S and C_2S in the samples indicate no complete hydration of

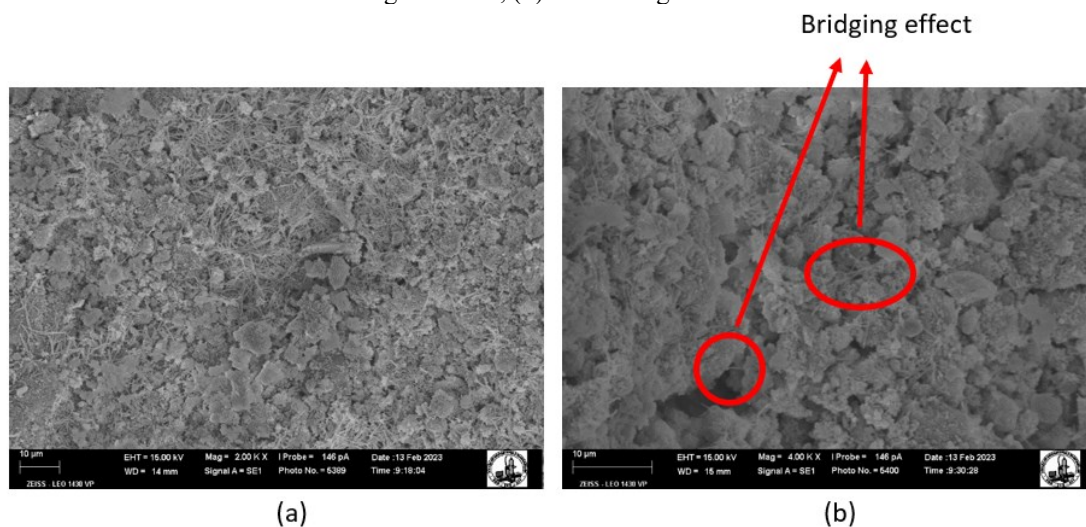
the Portland cement. In the particular case of slag, it is known that the hydration of C_2S and C_3S is much slower than that of cement, with part of these minerals being found unhydrated after 90 days of age (Wang; Yan, 2010). In this work, as the slag aggregates were ground for the preparation of the XRD samples, the C_2S inside these aggregates were accessed and therefore identified in the test. This result agrees with Franco de Carvalho et al. (2021), who performed the XRD of the same BOFS used in this work.

Figure 11 - SEM images of the cement matrix with NFC without sonication: (a) 2000x magnification, (b) 4000x magnification.



Source: The author (2024).

Figure 12 - SEM images of the cement matrix with NFC sonicated for 0.04 min/ml: (a) 2000x magnification, (b) 4000x magnification.



Source: The author (2024).

Some of the portlandite and the presence of calcite ($CaCO_3$) is attributed to the weathering and aging process that the residue has undergone. During this process, CaO

is stabilized and converted into portlandite and calcite (Martins et al., 2021). Lime (CaO) was also identified in the XDR, indicating that even the long period of weathering was not able to eliminate all the existing lime. The minerals brownmillerite (C₄AF) and wuestite observed in the XDR also come from the slag used. Franco de Carvalho et al. (2021) and Martins et al. (2022) performed XRD of the same slag used in this work, showing the presence of calcite, lime, and brownmillerite.

3.3.5. Eco-efficiency of composites

Table 4 shows the intensity of cement related to the eco-efficiency of the mixtures.

Table 4 - Consumption of materials and eco-efficiency of mixtures.

Time sonication (min/ml)	CI _c (kg/m ³ /MPa)	CI _f (kg/m ³ /MPa)
0	10.8	56.7
0.04	10.6	48.1
0.16	11.8	50.0
0.32	11.0	52.5

* CI_c : cement intensity for compressive strength; CI_f: cement intensity for flexural strength.

Source: The author (2024).

In the context of eco-efficiency, it is observed that sonication time has a minimal impact on the cement intensity for compressive strength. The obtained values range between 10.8 and 11.8 kg/m³/MPa, falling into the category of conventional concrete, where mixtures typically exhibit a cement intensity greater than 10 kg/m³/MPa (Grazia, 2023).

In terms of flexural strength, it is noted that the application of sonication effectively reduces the cement intensity required. Compared to the reference, the sonication time of 0.04 min/ml decreases the CI_f by 15.2%, and the sonication time of 0.16 min/ml decreases the CI_f by 11.8%. This implies that with sonication, achieving each additional 1 MPa in flexural strength demands less cement, thereby enhancing the eco-efficiency of the composites. Therefore, ensuring the proper dispersion of cellulose fibers improves the flexural properties of composites, allowing for a reduced cement consumption to achieve a targeted performance.

The consumption of cement of the composites was of 438.4 kg/m³. And due to the use of steel slag in place of aggregates, a waste consumption of 1997.6 kg/m³ of concrete was achieved. In terms of the volume of dry material, 80% of the composite is waste, proving that it is a product with a high rate of waste incorporation.

3.4. CONCLUSIONS AND FUTURE PERSPECTIVES

This study examined the impact of sonication time on NFC dispersion and the mechanical strength of cementitious composites with steel slag aggregate, yielding the following key conclusions:

- i. The UV-vis results revealed a significant disparity in absorbance between sonicated and non-sonicated samples. Given that more homogeneous solutions with smaller aggregates sediment less and thus present higher absorbance values, it can be inferred that sonication effectively enhanced the dispersion of NFCs.
- ii. The sonication of NFC solutions increased the zeta potential values of nanofibers compared to the reference. Non-sonicated samples can be characterized as slightly unstable based on their zeta potential. Conversely, sonicated samples exhibited zeta potentials ranging from -33.0 to -39.1 mV, indicating a moderate level of stability. In the context of producing cementitious composites, the stability of fibers in the aqueous medium is a relevant attribute to consider.
- iii. The workability of specimens during molding decreases with sonicated NFCs. Improved fiber dispersion results in a larger surface area, leading to increased water retention. This insight is important for adjusting the superplasticizer dosage to prevent mixtures with poor workability, making compaction and molding more challenging.
- iv. Sonication time had a positive impact on the flexural strength of the specimens. The most favorable outcomes were observed at times of 0.04 and 0.16 min/ml, showcasing strength gains of 17.9% and 13.4% compared to the reference. This finding aligns with other tests, suggesting that improved fiber dispersion has favored the bridging effect.
- v. Sonication of NFCs resulted in a reduction in the cement intensity of the specimens. This implies that achieving each MPa of flexural strength requires

less cement per volume of the mixture. Consequently, the enhanced dispersion of fibers through sonication contributes to an increased eco-efficiency of cementitious products.

- vi. After analyzing the mechanical, UV-vis, zeta potential, and eco-efficiency results, it is evident that sonication times of 0.04 min/ml and 0.016 min/ml yield the most effective dispersions and, consequently, higher mechanical strength. Considering the association of sonication time with sample volume, a recommendation for the production of the proposed cementitious material on a larger scale would be a sonication time of 0.04 min/ml. This choice would significantly reduce both the time required for composite production and energy consumption.

To optimize the fiber dispersion technique and enhance the eco-efficiency of cementitious composites containing steel slag and NFC, the following suggestions are proposed:

- i. Extend the investigation into the influence of sonication on fiber dispersion. It is advisable to explore how the NFC concentration in the solution might affect the sonication time for achieving improved dispersion.
- ii. Assess the effectiveness of incorporating surfactants and stabilizers into NFC dispersion and examine their impact on the eco-efficiency and mechanical strength of the resulting cement products.
- iii. Investigate the simultaneous application of sonication, surfactants, and/or stabilizers to ascertain potential synergistic effects between them. This exploration can provide insights into determining the most suitable methodology for achieving optimal NFC dispersion.

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CHAPTER 4: MECHANICAL PERFORMANCE OF CEMENTITIOUS COMPOSITES CONTAINING NANOFIBRILLATED CELLULOSE AND STEEL SLAG

Abstract: *The construction industry is pivotal for addressing societal needs like housing, infrastructure, and economic development. Yet, it poses environmental challenges due to resource exploitation and CO₂ emissions, mainly from cement production. To enhance sustainability, the study focused on two key strategies. Firstly, it incorporated basic oxygen furnace slag (BOFS) to reduce industrial waste disposal and natural resource consumption. Secondly, it introduced unbleached nanofibrillated cellulose (NFC) to boost strength and durability. Despite a reduction in mechanical strength with the substitution of cement by steel slag, this approach improved eco-efficiency by lowering cement intensity. NFCs significantly enhanced flexural strength, further optimizing eco-efficiency. The research achieved high-performance cementitious products, incorporating substantial waste content, maintaining mechanical strength, and demonstrating significant eco-efficiency gains. These findings contribute to a more sustainable construction industry by addressing environmental concerns and promoting the use of efficient materials.*

Keywords: Nanofibrillated celluloses, steel slag, cement-based composites, reuse of industrial waste, sustainable construction.

4.1. INTRODUCTION

Nanofibrillated cellulose (NFC) is a material that has garnered interest across various fields. It is renewable and serves as a sustainable alternative to petroleum-based products. Due to its characteristics, such as low density, high mechanical strength, and a high length-to-diameter ratio (Balea et al., 2019; Fukuzumi et al., 2009; Guimaraes et al., 2015; Josefsson, 2015), NFC has been employed to reinforce various matrices and films (Balea et al., 2016; Belbekhouche et al., 2011; do Lago et al., 2020; Kamel et al., 2020; Zhang et al., 2020). In the realm of building materials, NFCs have demonstrated promising results when integrated into cementitious composites, offering a pathway to create higher-performance and more sustainable materials (Santos et al., 2021). Different

mechanisms are identified to explain the contribution of nanofibrillated cellulose in cementitious matrices: (i) acting as nucleation points (Hoyos et al., 2019; Mejdoub et al., 2016; Onuaguluchi; Panesar; Sain, 2014), (ii) controlling cracks through a bridging effect (Correia et al., 2018; Fonseca et al., 2019), (iii) releasing water in a controlled manner during the curing process (Jiao et al., 2016), and (iv) creating a short-circuit effect that facilitates water access to the cement grains (Cao et al., 2015; Hoyos et al., 2019).

NFCs are typically derived from the disintegration of cellulose fibers through high-pressure processes. Various mechanical treatments can be employed for this disintegration, including high-pressure homogenizers or microfluidizers, ball mills, common refiners, steam explosion, ultrasonication, high-speed blenders, and others (Klemm et al., 2018; Santos et al., 2021). In most instances, a preliminary step in NFC production involves chemical processes such as delignification and bleaching to eliminate lignin from cellulose fibers (Santucci et al., 2016). The bleaching mechanism includes the oxidation of water-insoluble lignin, leading to the breakage of specific bonds and the formation of water-soluble compounds like aromatic aldehydes and carboxylic acids (Dai; Patti; Saito, 2016; Wang; Zhao, 2021). However, the use of unbleached NFCs is advantageous as it eliminates the need for this extra chemical treatment step, reducing costs and minimizing environmental impact (Santucci et al., 2016). Therefore, the promotion of the application of unbleached NFC is encouraged.

Another material under study for the production of cementitious composites is basic oxygen furnace slag (BOFS). This residue originates from the steel production process in a Linz-Donawitz (LD) oxygen converter (Yildirim; Prezzi, 2011), formed by the combination of oxygen with lime, dolomite, and iron, along with impurities from the scraps added to the converter (Shi, 2004). The composition of steel slag varies based on the raw materials used in steel production. In general, four oxides constitute the majority of the residue's composition: lime (CaO), periclase (MgO), silica (SiO₂), and wustite (FeO) (Martins et al., 2021; SHI, 2004).

The global crude steel production in 2020 reached 1878 million tons, with China as the leading producer and Brazil ranking ninth (Worldsteel Association, 2021). Given that each ton of steel production results in 100-150 kg of BOFS (Fernández-González et al., 2019), it's evident that a massive volume of waste is generated. Therefore, it is imperative to explore viable alternatives to utilize this residue, preventing its disposal in landfills and mitigating environmental issues (Martins et al., 2021).

In construction, BOFS can serve as an aggregate (Aparicio; Hernández; Anaya, 2020; Guo et al., 2018, 2019), contributing to increased mechanical strength in cementitious composites. This is attributed to the greater angularity of slag aggregates, which often possess characteristics comparable to, and sometimes even superior to, conventional aggregates (Geiseler, 1996; Qasrawi, 2014). Another approach involves using finely ground slag as a supplementary cementing material, potentially acting as a partial substitute for cement (Franco de Carvalho et al., 2019, 2020; Han; Zhang, 2018; Martins et al., 2022; Shi et al., 2015). Reducing cement consumption carries significant environmental benefits, given that the cement industry is a major emitter of CO₂ (Benhelal; Shamsaei; Rashid, 2021). However, it's worth noting that the cementing activity of BOFS is slower than that of cement (Wang et al., 2018), and the use of super-fine steel slag may be uneconomical and could lead to durability issues due to expansion into the composite's matrix (Franco de Carvalho et al., 2019; Wang; Yang; Yan, 2013).

The existing body of literature lacks explorations into the potential synergistic effects arising from the combination of NFCs and BOFS aggregates within cementitious composites. Despite extensive research into the individual impacts of these components on cementitious matrices, the specific microstructural effects provided by NFCs and BOFS remain unknown. In addition, there is a gap in the technical literature regarding the application of central composite design methods to obtain response surfaces that describe the performance of mortars containing NFCs and BOFS.

In this research, the authors investigated the influence of partially replacing cement with BOFS powder and introducing NFCs into the cementitious matrices. The incorporation of nanocellulose to improve the mechanical performance of cementitious matrices with slag was not found in the literature research, which highlights the relevance and timeliness of this work. The ultimate aim is to develop a product with high residue incorporation and satisfactory mechanical performance, thus contributing to a more sustainable construction industry. The novelty of the work is threefold: (i) the compressive strength, flexural strength, microstructure and eco-efficiency of cementitious composites containing NFCs and BOFS were reported by the first time; (ii) novel discussions related to variations in the packing factor of mortars produced using partial replacement of cement by BOFS and addition of different dosages of NFCs; and (iii) first evaluation of the technical feasibility of using the face-centered central composite design to statically investigate synergies and antagonisms within mixtures of NFCs and BOFS.

4.2. MATERIAL AND METHODS

4.2.1. Materials

The NFC used in this study was unbleached nanofibrillated cellulose sourced from Pinus, obtained through a delamination process. The material was manufactured and provided by Embrapa Florestas, situated in Colombo, Brazil. The characterization of NFC gel and fibers was conducted as explained in Chapter 3. Table 1 displays the properties of both the first and second batches of gel supplied by Embrapa Florestas. The first batch was used in the initial part of the work to define the ideal packing factor. The second batch was used in experimental design to evaluate the mechanical strength and eco-efficiency of the composites produced.

Table 1 - Properties of the NFCs used in the research.

	NFC – batch 1	NFC – batch 2
Gel concentration (%)	2.78	1.08
Gel specific gravity (g/cm ³)	≅ 1	≅ 1
NFC specific gravity (g/cm ³)	1.09	1.08

Source: The authors (2024).

In the production of the cementitious composites, CPV-ARI cement, corresponding to ASTM type III, was used. This cement, known for its low incorporation of mineral additions (ABNT, 2018), had its specific gravity measured at 3.05 g/cm³ using the ABNT NBR 16605 method (ABNT, 2017).

The fine aggregates were obtained from BOFS supplied by the Arcelor-Mittal Company, and they underwent a five-year weathering process in the Laboratory of Civil Construction Materials patio at the Federal University of Ouro Preto - UFOP, Brazil. This weathering procedure was conducted to stabilize the expansive oxides present in BOFS. The original BOFS featured particles ranging between 6.35 and 12.5 mm, a gray color, and a specific gravity of 3.57 g/cm³, as characterized by Martins et al. (Martins et al., 2022). The fine aggregates of BOFS were produced as explained in Chapter 3. The raw and dried slag was ground in a Los Angeles equipment for 40 min. Then, the material was sieved, using the portion passing through the 2.36 mm aperture sieve as fine aggregate. The material retained was ground to produce slag powder to be used in the work as a partial

replacement for cement. This processing was also carried out on the Los Angeles equipment for 120 min. Then, the material generated was sieved, with the fraction passing through the sieve with an opening of 0.15 mm used as slag powder to produce the specimens.

To provide appropriate workability of the composites, a polycarboxylate-based superplasticizer (SP) admixture (MC-PowerFlow 4001) was employed.

4.2.2. Preparation of the cementitious composites

Using the modified Andreassen curve as a reference, the mixtures comprised 20% cement and 80% BOFS sand by volume, forming a 1:4 mixture. Starting from this reference, various amounts of NFC were added (0; 0.1; 0.2; 0.3; 0.4, and 0.5% in relation to the cement mass), along with different packing factors (0.68; 0.70; 0.72; and 0.75). In this context, the packing factor (ϕ) represents the ratio between the volume of dry material in the mixture and the total produced volume. Hence, a higher packing factor implies a reduced amount of water used. Workability was maintained within the flow diameter range of 8.5-10.5 cm by adjusting the superplasticizer content. Flow diameters were obtained by the mini-slump test as described in Chapter 3. Thus, the molding and compaction conditions were kept similar across all mixtures. The details of these mixtures are presented in Table 2.

Table 2 - Mass proportions of the mixtures.

Mixture	Cement	BOFS sand	SP	NFC	Water
REF-0.68	1	4.86	0	0	0.772
0.1NFC-0.68	1	4.86	0.010	0.001	0.764
0.2NFC-0.68	1	4.86	0.020	0.002	0.755
0.3NFC-0.68	1	4.86	0.030	0.003	0.747
0.4NFC-0.68	1	4.86	0.040	0.004	0.738
0.5NFC-0.68	1	4.86	0.050	0.005	0.730
REF-0.70	1	4.86	0.005	0	0.699
0.1NFC-0.70	1	4.86	0.020	0.001	0.686
0.2NFC-0.70	1	4.86	0.030	0.002	0.677
REF-0.72	1	4.86	0.01	0	0.625
0.1NFC-0.72	1	4.86	0.025	0.001	0.621
0.2NFC-0.72	1	4.86	0.045	0.002	0.608
REF-0.75	1	4.86	0.015	0	0.500
0.1NFC-0.75	1	4.86	0.020	0.001	0.500
0.2NFC-0.75	1	4.86	0.035	0.002	0.500

Source: The authors (2024).

For the production of the mixtures, water and the NFC gel were initially sonicated for 0.04 minutes per ml of solution, following the methodology explained in Chapter 3. A probe sonicator with a power of 50W and a frequency of 20 kHz was employed for this step. Subsequently, the superplasticizer was added, and the solution was shaken for 30 seconds using an electric mixer. The cement and BOFS sand, previously mixed while still dry, were then gradually introduced into the mixer and stirred for 10 minutes. Following the addition of the dry materials, the mixture was stirred for an additional 5 minutes. Using the resulting mixture, prismatic specimens with dimensions of 2 cm x 2 cm x 8 cm were molded. The compaction of the material was carried out on a vibrating table in two layers, with each layer taking 15 seconds. The specimens were then cured in a moist room under controlled conditions: 23 ± 2 °C and 95% humidity (Figure 1). At 28 days, three specimens of each test mixture were evaluated for flexural and compressive strength, according to the ABNT NBR 13279 (ABNT, 2005).

Figure 1 - Production of specimens for compression and bending tests. From left to right: REF-0.72; 0.1NFC-0.72 and 0.2NFC-0.72.



Source: The authors (2024).

4.2.3. Design of experiments (DOE)

A Design of Experiments (DOE) is a systematic statistical methodology that enables the understanding of how various parameters can impact the response variables of a process or product. Its advantage lies in its ability to generate information and results with minimal experimentation (Wagner; Mount; Giles, 2014).

Various experimental designs can be employed to analyze factors and create a response surface. One such design is the central composite design, distinguished by points at the center of the experimental domain and star points outside this domain, facilitating the estimation of the curvature of the response surface. In the specific case of the face-

centered design, the star points are positioned on the face of the experimental domain, necessitating three levels per analyzed factor (Amir; Pougnet; Hami, 2020).

From the reference mixture obtained in the previous studies with a packing factor of 0.72, eight additional mixtures were defined following a central composite face-centered design (CCF). The independent variables considered were: (X_1) NFC addition content, with values of 0%, 0.1%, and 0.2% in relation to the cement weight of the reference mixture; (X_2) BOFS powder/cement ratio, with values of 0%, 25%, and 50% (Table 3).

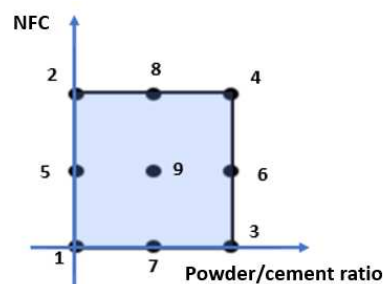
For each mixture within the experimental design, four repetitions were conducted for the bending test and eight repetitions for the compression test (utilizing the halves obtained in the bending test). The results were subject to a statistical analysis using Minitab 18 software. Following the analysis, a response surface was generated, representing the shaded area on the graph depicted in Figure 2.

Table 3 - Central composite face-centered design (CCF).

Mixture	X_1 (NFC - %)		X_2 (powder/cement - %)	
1	(-1)	0.00	(-1)	0
2	(+1)	0.50	(-1)	0
3	(-1)	0.00	(+1)	50
4	(+1)	0.50	(+1)	50
5	(0)	0.25	(-1)	0
6	(0)	0.25	(+1)	50
7	(-1)	0.00	(0)	25
8	(+1)	0.50	(0)	25
9	(0)	0.25	(0)	25
9	(0)	0.25	(0)	25
9	(0)	0.25	(0)	25

Source: The authors (2024).

Figure 2: Position of mixtures on the response surface.



Source: The authors (2024).

The response surface methodology encompasses a set of statistical and mathematical techniques designed to fit experimental data into linear or polynomial empirical models. Once the empirical model is derived, it can be visually represented through an n-dimensional surface (Bezerra et al., 2008). In the case of two factors, X1 (% NFC) and X2 (% BOFS powder/cement ratio), a first or second-order model can be established, with or without double interaction between the terms. The complete model is represented by Eq. (1), where y is the response variable, β_n the regression coefficients, x_i the independent variables, and ε the residual associated with the experiment.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

4.2.4. Evaluation of mechanical performance in cementitious composites

The concrete mixtures produced according to the Design of Experiments (DOE) were characterized for compressive and flexural strength (ABNT, 2005; ASTM, 2014, 2018) at 7, 28, and 56 days.

Another parameter evaluated was the eco-efficiency of the composites, following the methodology proposed by Damineli et al. (Damineli et al., 2010; Damineli; Pileggi; John, 2013). The binder intensity (bi) can be calculated from Eq. (2), where b is the total binder consumption (in kg/m^3) and p is the composite performance requirement.

$$bi = \frac{b}{p} \quad (2)$$

In this study, the cement intensity for compressive strength (CI_c) was according to Eq. (3). Additionally, as fibers tend to enhance the flexural performance of cementitious composites, the cement intensity for flexural strength (CI_f), was also calculated using Eq. (4). In these equations, c represents the total cement consumption (in kg/m^3), p_c denotes the performance in compression (compressive strength at 28 days, in MPa), and p_f represents the performance in bending (flexural strength at 28 days, in MPa).

$$CI_c = \frac{c}{p_c} \quad (3)$$

$$CI_f = \frac{c}{p_f} \quad (4)$$

By definition, CI_c and CI_f are the cement consumption required to achieve 1 MPa of compressive and flexural strength at 28 days, respectively. Therefore, lower values indicate higher eco-efficiency in the mixtures.

4.2.5. Microstructural evaluation

SEM images were captured using the Leo 1430 VP Scanning Electron Microscope, located in the Nucleus of Microscopy and Microanalysis at the Federal University of Viçosa (UFV). The samples utilized were small pieces of specimens with interrupted hydration after 28 days of curing with isopropyl alcohol, following the recommendations of Scrivener et al. (2018). To improve conductivity, the samples were adhered to the stub using carbon tapes and then metallized with gold.

To assess the compounds present in the 28-day-old specimens, an X-ray diffraction (XRD) analysis was performed. The scanning range (2θ) covered from 10° to 80° , and the D8 Discover diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was utilized. The step size was 0.05° and the accumulated time per step was 1 s.

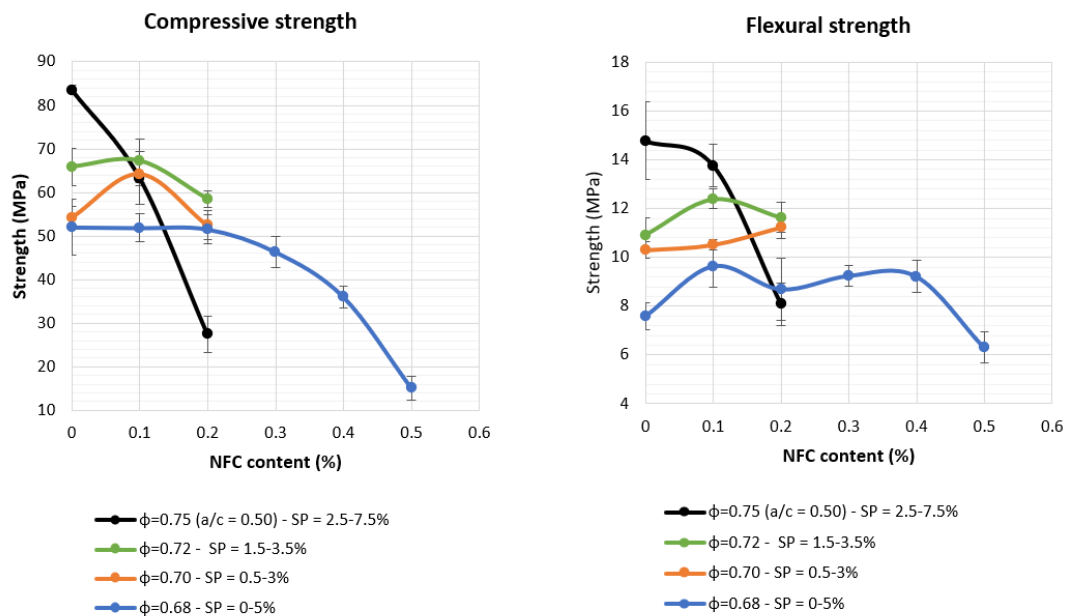
4.3. RESULTS AND DISCUSSION

4.3.1. Influence of the packing factor

Figure 3 shows the results of compressive and flexural strength at 28 days for different packing factors. Observing this results, it becomes evident that as the packing factor increases (and, consequently, the water content decreases), the mechanical performance of the mixtures was improved. This correlation between the water/cement ratio and the strength of cementitious materials is well-established in the literature. The phenomenon is defined by a matrix weakening due to increased porosity as the water/cement ratio rises (Mehta; Monteiro, 2006). While drier mixtures exhibit greater

strength, their low workability poses challenges in molding and compacting the specimens.

Figure 3 - Variation of compressive and flexural strength for different packing factors.



Source: The authors (2024).

The NFC content is another factor that significantly decreases workability (Machado et al., 2017; Nassiri et al., 2021; Sun et al., 2016). The fibers readily entangle within the matrix, creating a network structure that hinders the movement of cement particles and elevates the mixture's viscosity (Tang et al., 2019). Additionally, water sequestration by NFCs, held by hydrogen bonds on their surface, decreases the available water for lubricating the cement particles.

As fibers tend to reduce the workability of mixtures, water-reducing additives are commonly employed to restore their workability (Goncalves; Boluk; Bindiganavile, 2021). This approach was adopted in this study, where the superplasticizer content varied among mixtures to maintain similar workability levels. Consequently, the water-to-cement ratio and compaction were kept constant during the evaluation. For mixtures with a packing factor of 0.75 and additions of 0.1% and 0.2% NFC, substantial amounts of superplasticizer (4.5% and 7.5% relative to the cement mass, respectively) were necessary. Greater amounts of superplasticizer can increase air content and exudation in concrete, delay setting time, increase porosity, and negatively impact mechanical strength, especially at early ages (Zhao et al., 2020). Therefore, these mechanisms can

explain the abrupt drop in mechanical strength in samples with 0.1% and 0.2% NFC (Table 4).

In mixtures with lower packing factors, allowing the use of superplasticizer content within manufacturers' recommendations (below 5% by mass of cement), no abrupt decline in strength was observed with increasing fiber content as observed in $\phi = 0.75$. In fact, adding small amounts of fibers appears to enhance both flexural and compressive strength. For instance, in mixtures with $\phi = 0.72$, there was a 2% increase in average compressive strength with 0.1% NFC compared to the reference mix. The average flexural strength increased by 13.5% and 6.5% with additions of 0.1% and 0.2% NFC, respectively. Similarly, in mixtures with $\phi = 0.70$, a gain of 18.5% in compressive strength was observed with 0.1% NFC, along with a 2% and 9% increase in flexural strength for additions of 0.1% and 0.2% NFC, respectively.

For mixtures with $\phi = 0.68$, having a higher water content allowed for the incorporation of higher NFC concentrations (0.3%, 0.4%, and 0.5%). However, a noticeable reduction in compressive strength became significant with fiber additions exceeding 0.4%, and for flexural strength, it was evident with the addition of 0.5% NFC

The results suggest that fibers are advantageous in lower concentrations. According to the literature, the NFCs can promote the hydration of cement particles and aid in crack control (Bakkari et al., 2019; Hissaine et al., 2020; Hoyos et al., 2019). However, they agglomerate in larger quantities and form points of weakness in the matrix, impairing the mechanical strength (Mejdoub et al., 2016; Onuaguluchi; Panesar; Sain, 2014; Sun et al., 2016).

Due to the substantial deviations in the results, certain outcomes of the Tukey tests showed no statistically significant difference between the evaluated factors. Nevertheless, the mixtures containing fibers consistently exhibited higher averages compared to the reference. Table 4 to Table 11 show the statistical results of all traits.

Table 4 - Tukey test for the compressive strength of mixtures with $\phi = 0.75$ (significance level of 5%).

Mixture	N	Mean	Grouping
REF-0.75	5	83.530	A
0.1NFC-0.75	6	63.34	B
0.2 NFC-0.75	6	27.43	C

Source: The authors (2024).

Table 5 - Tukey test for the flexural strength of mixtures with $\phi = 0.75$ (significance level of 5%).

Mixture	N	Mean	Grouping
REF-0.75	3	14.768	A
0.1 NFC-0.75	3	13.763	A
0.2 NFC-0.75	3	8.078	B

Source: The authors (2024).

Table 6 - Tukey test for the compressive strength of mixtures with $\phi = 0.72$ (significance level of 5%).

Mixture	N	Mean	Grouping
0.1 NFC-0.72	6	67.32	A
REF-0.72	6	65.94	A
0.2 NFC-0.72	6	58.515	B

Source: The authors (2024).

Table 7 - Tukey test for the flexural strength of mixtures with $\phi = 0.72$ (significance level of 5%).

Mixture	N	Mean	Grouping
0.1 NFC-0.72	3	12.393	A
0.2 NFC-0.72	3	11.636	A
REF-0.72	3	10.921	A

Source: The authors (2024).

Table 8 - Tukey test for the compressive strength of mixtures with $\phi = 0.70$ (significance level of 5%).

Mixture	N	Mean	Grouping
0.1 NFC-0.70	6	64.27	A
REF-0.70	6	54.24	B
0.2 NFC-0.70	6	52.43	B

Source: The authors (2024).

Table 9 - Tukey test for the flexural strength of mixtures with $\phi = 0.70$ (significance level of 5%).

Mixture	N	Mean	Grouping
0.2 NFC-0.70	3	11.222	A
0.1 NFC-0.70	3	10.516	A B
REF-0.70	3	10.301	B

Source: The authors (2024).

Table 10 - Tukey test for the compressive strength of mixtures with $\phi = 0.68$ (significance level of 5%).

Mixture	N	Mean	Grouping
REF-0.68	6	52.03	A
0.1 NFC-0.68	6	51.87	A
0.2 NFC-0.68	6	51.56	A
0.3 NFC-0.68	6	46.36	A
0.4 NFC-0.68	6	36.03	B
0.5 NFC-0.68	6	15.09	C

Source: The authors (2024).

Table 11 - Tukey test for the flexural strength of mixtures with $\phi = 0.68$ (significance level of 5%).

Mixture	N	Mean	Grouping
0.1 NFC-0.68	3	9.639	A
0.3 NFC-0.68	3	9.243	A
0.4 NFC-0.68	3	9.216	A
0.2 NFC-0.68	3	8.695	A
REF-0.68	3	7.587	A B
0.5 NFC-0.68	3	6.303	B

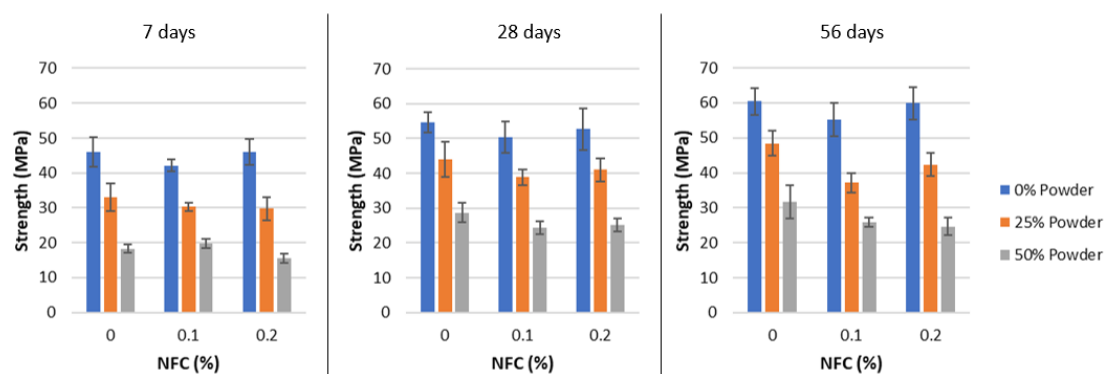
Source: The authors (2024).

The most recommended mixtures are those capable of achieving a balance among: (i) a high packing factor, (ii) superplasticizer levels within the manufacturer's recommendations, and (iii) workability conducive to effective molding and compaction. However, this equilibrium is influenced by the fiber content, with higher amounts negatively impacting workability. Therefore, based on the obtained results, the addition of fibers up to 0.2% by cement mass and a packing factor of 0.72 proved to be interesting parameters for a more in-depth evaluation using an experimental design.

4.3.2. Evaluation of the mechanical properties of composites by CCF

The results of the compressive strength tests are shown in Figure 4.

Figure 4 - Results of compressive strength of the studied composites.



Source: The authors (2024).

The observed decrease in compressive strength with an increase in residue content aligns with findings noted by Wang et al. (Wang et al., 2013) and Han and Zhang (Han; Zhang, 2018). These authors observed a similar phenomenon when considering mixtures with identical water-to-cement ratios. Cement replacements with slag at levels of 15%,

30%, and 45% resulted in diminished mechanical strength and more pronounced shrinkage, porosity, permeability to chloride ions, and carbonation. The lower reactivity of slag powder compared to cement may explain these outcomes (Han et al., 2015).

Concerning fiber content, the influence of NFCs is not as evident as that of the BOFS powder content. Compressive strengths remain comparable when analyzing mixtures with the same BOFS powder content, showing a slight tendency to decrease with increasing fiber content, particularly in mixtures with 0.1% NFC. Table 12, Table 13, and Table 14 present the Tukey test results for mixtures with identical BOFS powder content.

Table 12 - Tukey test for the compressive strength of mixtures with 0% powder (significance level of 5%).

Mixture	N	Mean	Grouping
REF	8	54.59	A
0.2% NFC	8	52.64	A
0.1% NFC	8	50.43	A

Source: The authors (2024).

Table 13 - Tukey test for the compressive strength of mixtures with 25% powder (significance level of 5%).

Mixture	N	Mean	Grouping
REF	8	43.98	A
0.2% NFC	8	40.97	A B
0.1% NFC	7	38.88	B

Source: The authors (2024).

Table 14 - Tukey test for the compressive strength of mixtures with 50% powder (significance level of 5%).

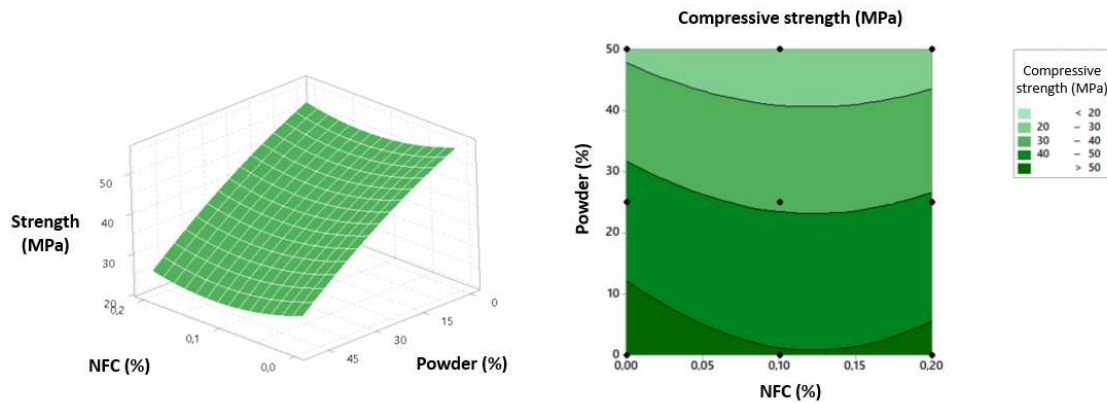
Mixture	N	Mean	Grouping
REF	8	28.68	A
0.2% NFC	8	25.15	B
0.1% NFC	8	24.37	B

Source: The authors (2024).

The influence of NFC and slag powder content becomes more apparent when examining the response surface (Figure 5) derived from the central composite face-centered design. Eq. (5) provides non-coded coefficients that can be directly applied to determine compressive strength (Y_c) based on NFC and BOFS powder contents (in %). Eq. (6) also presents coded coefficients, enabling a direct comparison of the factors'

effects, as the variation range of the equation terms is standardized. Thus, the difference in scale between the BOFS powder/cement content (0 – 50%) and NFC (0 – 0.2%) does not affect the interpretation of the influence of each factor. The powder/cement and NFC values used in this equation are dimensionless, ranging from -1 to +1, whose correspondence with the real values is shown in Table 3.

Figure 5: Surface plot and contour plot of the compressive strength at 28 days.



Source: The authors (2024).

$$Y_c = 54.998 - 76.23 \cdot NFC - 0.3721 \cdot Powder + 310.5 \cdot NFC^2 - 0.003151 \cdot Powder^2 \quad (5)$$

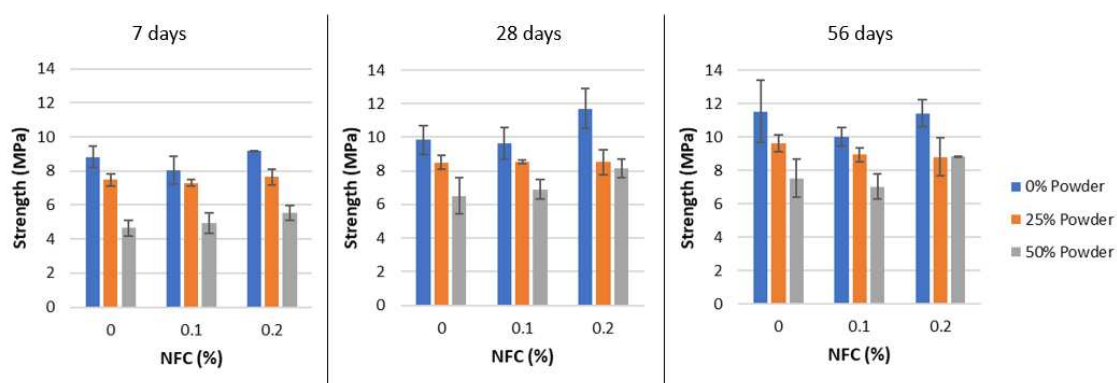
$$Y_c = 39.209 - 1.413 \cdot NFC - 13.241 \cdot Powder + 3.105 \cdot NFC^2 - 1.970 \cdot Powder^2 \quad (6)$$

The quadratic equation exhibits a high coefficient of determination ($R^2 = 99.91\%$) and elucidates the impact of BOFS powder and NFC on compressive strength. It's apparent that when considered individually, both factors contribute to a reduction in strength. The BOFS powder content holds greater significance in the strength decrease (coefficient -13.241) than the NFC content (coefficient -1.413). However, the quadratic term corresponding to NFC introduces a strength increase (coefficient +3.105). This term generates the parabolic isolines on the contour plot, suggesting a trend that increasing fiber content could enhance composite performance. If validated in future studies, this increasing trend would align with findings in the literature where increased fiber content has been associated with improvements in compressive strength (Barnat-Hunek et al., 2019; Dai et al., 2015; Mejdoub et al., 2016).

Regarding flexural behavior, the results are presented in Figure 6. There is a general decline in flexural strength with an increasing incorporation of slag powder in the

mixtures. Regarding fiber content, the addition of NFC is observed to enhance mechanical strength. At 28 days, in mixtures without BOFS powder, a 19% increase in flexural strength was noted with the addition of 0.2% NFC. In mixtures with 50% BOFS powder, this increase reached 25% in specimens with 0.2% NFC. However, in mixtures with 25% BOFS powder, the difference was not significant. Table 15, Table 16, and Table 17 present the Tukey test results for mixtures with the same BOFS powder content. These findings align with similar results in the literature, where an increase in fiber content is associated with improvements in flexural strength. This is attributed to NFCs favoring matrix hydration and controlling crack propagation through a bridging effect (Fonseca et al., 2019; Kamasamudram; Ashraf; Landis, 2020; Onuaguluchi; Panesar; Sain, 2014; Reixach et al., 2019).

Figure 6 - Results of flexural strength of the studied composites.



Source: The authors (2024).

Table 15 - Tukey test for the flexural strength of mixtures with 0% powder (significance level of 5%).

Mixture	N	Mean	Grouping
0.2% NFC	4	11.698	A
REF	4	9.844	A B
0.1% NFC	4	9.642	B

Source: The authors (2024).

Table 16 - Tukey test for the flexural strength of mixtures with 25% powder (significance level of 5%).

Mixture	N	Mean	Grouping
0.1% NFC	4	8.543	A
0.2% NFC	4	8.511	A
REF	4	8.490	A

Source: The authors (2024).

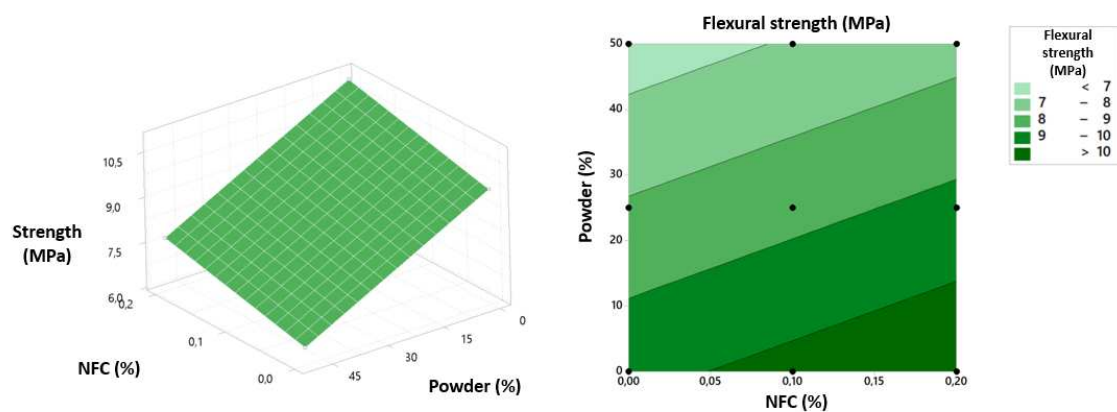
Table 17 - Tukey test for the flexural strength of mixtures with 50% powder (significance level of 5%).

Mixture	N	Mean	Grouping
0.2% NFC	4	8.135	A
0.1% NFC	4	6.900	A B
REF	4	6.508	B

Source: The authors (2024).

Figure 7 illustrates the response surface and contour plot for flexural strength (Y_f). The influence of BOFS powder and NFC contents can be described by a linear equation with uncoded (Eq. (7)) or coded (Eq. (8)) coefficients, achieving an R^2 of 89.22%. According to Eq. (8), it is evident that BOFS powder has a more substantial impact on the composite, leading to a decrease in strength, while NFC contributes positively.

Figure 7: Surface plot and contour plot of the flexural strength at 28 days.



Source: The authors (2024).

$$Y_f = 9.720 + 5.84 \cdot NFC - 0.06427 \cdot Powder \quad (7)$$

$$Y_f = 8.697 + 0.584 \cdot NFC - 1.607 \cdot Powder \quad (8)$$

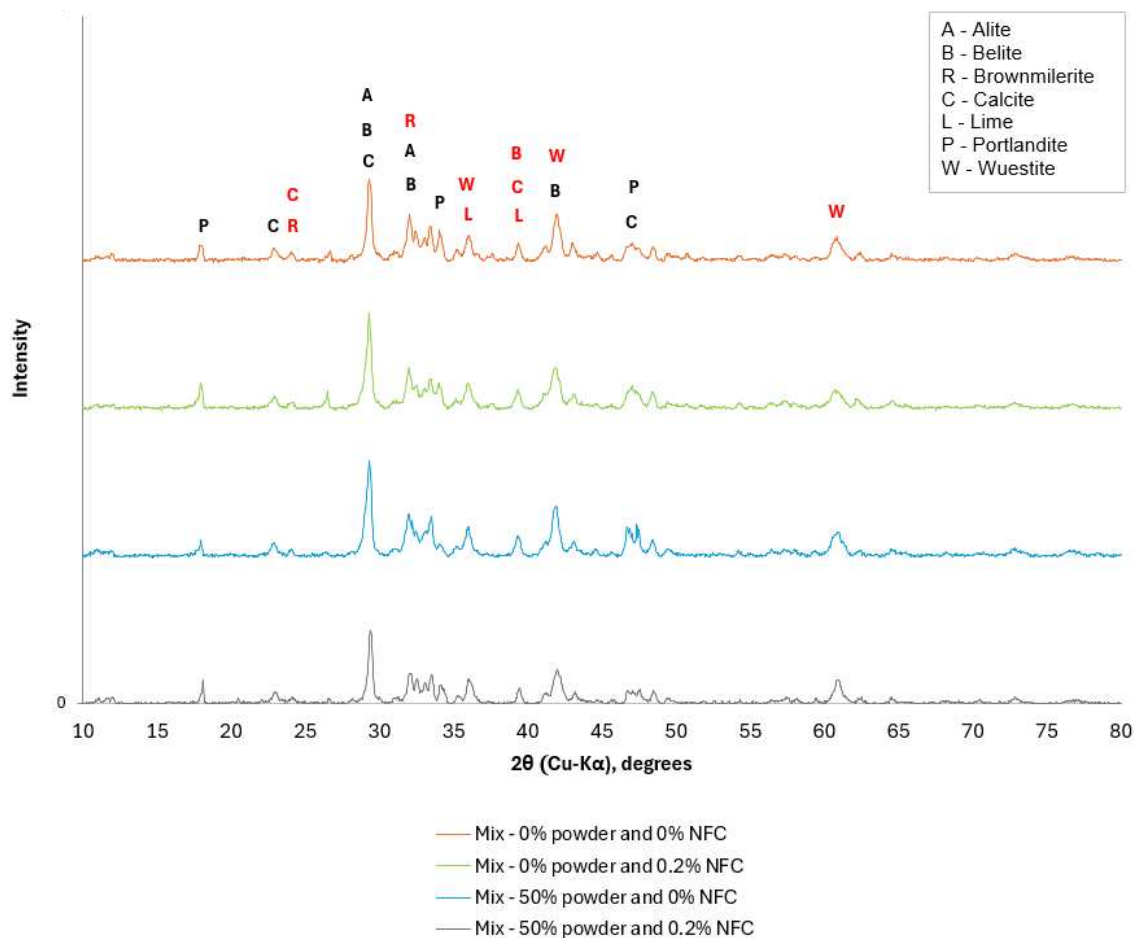
4.3.3. Microstructural evaluation

Figure 8 displays the XRD results for four mixtures with extreme values of BOFS powder and NFC. The identified peaks are similar to those found in Chapter 3. Through a qualitative analysis, it is observed that the XRD peaks are similar, suggesting no variation in the types of hydrated compounds among the different samples. This finding may clarify why mixtures with the same BOFS powder content exhibit very similar

compressive strengths. The enhanced flexural strength in mixtures with NFC could be attributed to the bridging effect.

In mixtures with a higher replacement of cement with BOFS powder, lower mechanical strength was observed, a phenomenon attributed in the literature to the reduced reactivity of slag, leading to a more porous matrix and increased susceptibility to shrinkage (Han et al., 2015; HAN; Zhang, 2018; Wang et al., 2013). In future work, a study will be conducted to investigate the variations in hydration between samples with different levels of cement replacement by BOFS powder and the potential interference of NFCs in this process.

Figure 8 - Results of XRD analysis of cementitious composites.

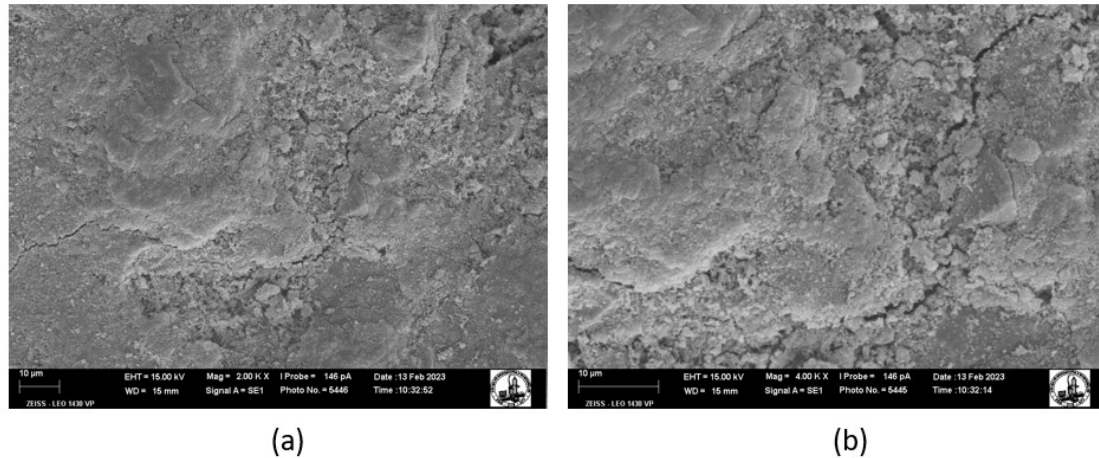


Source: The authors (2024).

Figure 9 and Figure 11 depict the SEM images of samples without the addition of NFC and with 0% and 50% BOFS powder/cement, respectively. Figure 10 and Figure 12 show images with 0.2% NFC and with 0% and 50% BOFS powder/cement, respectively.

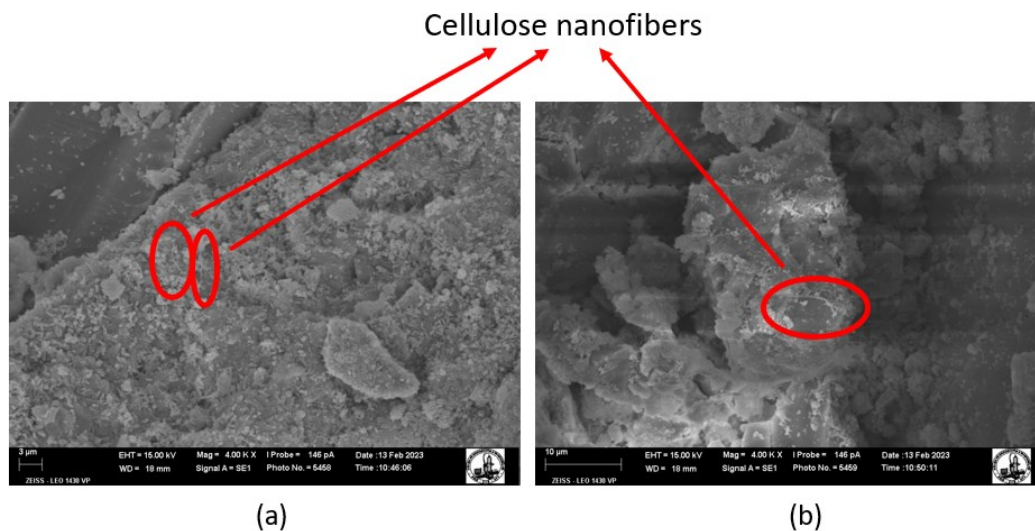
The NFC fibers are identifiable, especially in Figure 12, where the bridging effect is evident. These images elucidate the observed gain in flexural strength in the previous section, as NFCs aid in minimizing crack propagation, thereby enhancing flexural strength.

Figure 9 - SEM image of sample with 0% NFC and 0% BOFS powder: (a) 2000x magnification; (b) 4000 x magnification.



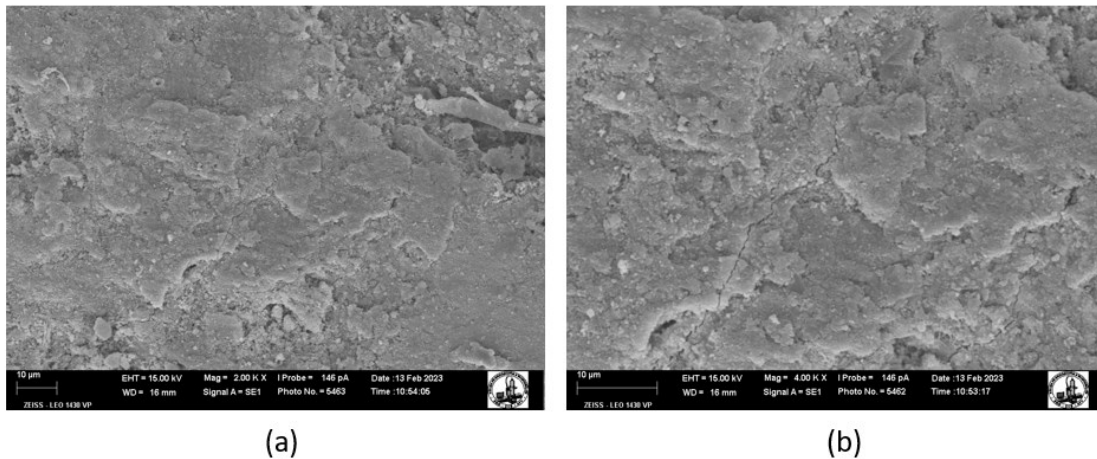
Source: The authors (2024).

Figure 10 - SEM image of sample with 0.2% NFC and 0% BOFS powder: (a) and (b) 4000 x magnification.



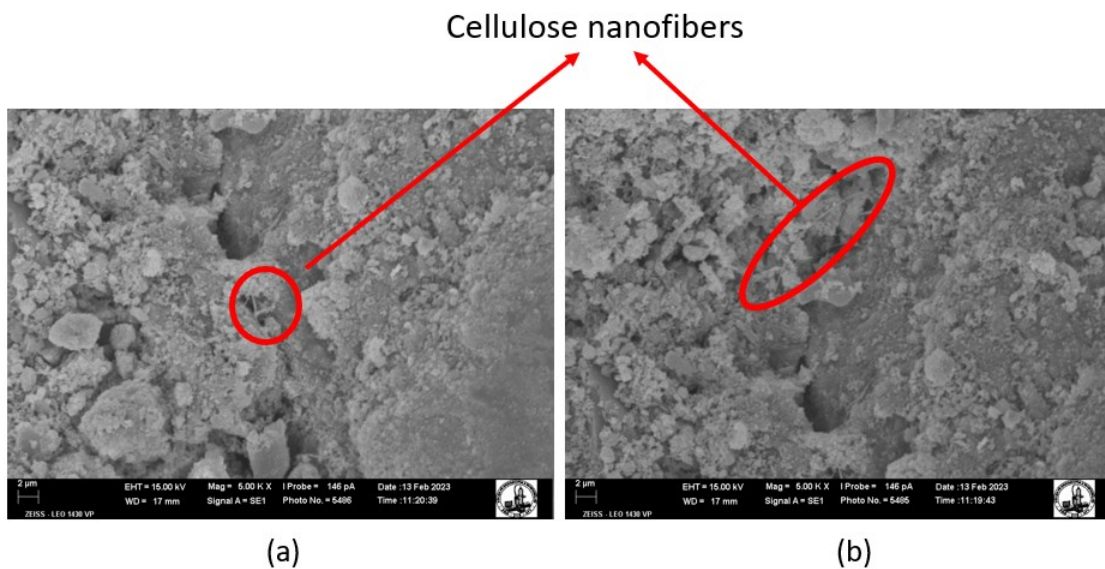
Source: The authors (2024).

Figure 11 - SEM image of sample with 0% NFC and 50% powder: (a) 2000x magnification; (b) 4000 x magnification.



Source: The authors (2024).

Figure 12 - SEM image of sample with 0.2% NFC and 50% powder: (a) and (b) 5000 x magnification.



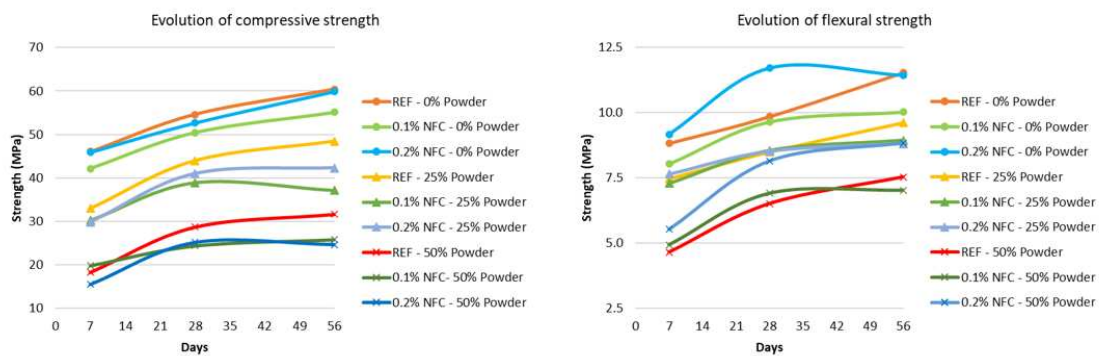
Source: The authors (2024).

4.3.4. Evolution of strength over time

For compressive strength, a discernible pattern of strength gain is observed as the age of the specimens progresses (Figure 13), as expected. The strength increase in mixtures without BOFS powder is more pronounced, with increments of 10.6%, 9.3%, and 13.7% for 0%, 0.1%, and 0.2% of NFC, respectively, between 28 and 56 days. Moreover, the strength increases from 7 to 56 days. In contrast, for mixtures with 25% and 50% BOFS powder, only the reference maintains strength growth over time, while

mixtures with fiber stabilize after 28 days. One possible explanation for this stabilization could be the crystallization of cellulose fibers in an alkaline environment, making them more fragile (Wei; Meyer, 2015). The presence of powder may enhance this crystallization, a topic that will be investigated in future research.

Figure 13 - Evolution of mechanical strength over time.



Source: The authors (2024).

A similar trend is observed for flexural strength. However, it is noteworthy that the concentration of 0.2% NFC in mixtures with BOFS powder appears to enhance the strength increase from 7 to 28 days compared to the reference. In this time interval, the reference mixtures with 0% BOFS powder exhibit a strength gain of 11.6%, while the mixture with 0.2% NFC shows a gain of 27.7%. Additionally, the reference mixtures with 50% BOFS powder have a strength gain of 40.0%, while the mixture with 0.2% NFC shows an increase of 47.5%. Nanofibers may be contributing to crack containment, thus favoring mechanical strength, as illustrated in Figure 12. NFC can also interfere with the hydration rate of cement and powder compounds, which will be verified in future work about the hydration kinetics of the developed composites.

4.3.5. Eco-efficiency of composites

Table 18 displays the consumption of cement and waste, along with the intensity of cement in relation to the eco-efficiency of the mixtures.

The cement intensity for compression ranges between 9.5 and 14.1 kg/m³/MPa. These values fall within the range reported in the literature for conventional concrete, which is 9 to 14 kg/m³/MPa (Campos et al., 2020; Grazia et al., 2019). The results for cement intensity in bending reveal the positive impact of incorporating BOFS powder

and adding NFC on enhancing the eco-efficiency of composites. Specifically, the mixture containing 0.2% NFC and 50% BOFS powder exhibits a 40% lower cement intensity in bending CI_f compared to the reference mixture without BOFS powder. It is worth emphasizing that although the addition of BOFS powder reduces the absolute strength of the composites, the proportion of reduction in cement consumption is greater than the loss of strength. Thus, it is possible to produce a more sustainable composite, and still with adequate strength for use in civil construction.

Table 18 - Consumption of materials and eco-efficiency of mixtures.

Mixture	Cement consumption (kg/m ³)	CI_c (kg/m ³ /MPa)	CI_f (kg/m ³ /MPa)	Powder consumption (kg/m ³)	Waste consumption (kg/m ³)	Volume of waste incorporation (%)
REF - 0% powder	438.6	9.5	44.6	0	1998.7	80
0.1% NFC - 0% powder	438.4	10.4	45.5	0	1997.6	80
0.2% NFC - 0% powder	438.1	9.5	37.5	0	1996.5	80
REF - 25% powder	329.0	10.0	38.7	133.6	2132.3	85
0.1% NFC - 25% powder	328.8	10.9	38.5	133.5	2131.1	85
0.2% NFC - 25% powder	328.6	11.0	38.6	133.4	2129.9	85
REF - 50% powder	219.3	12.0	33.7	267.1	2265.8	90
0.1% NFC - 50% powder	219.2	11.1	31.8	267.0	2264.6	90
0.2% NFC - 50% powder	219.1	14.1	26.9	266.8	2263.3	90

Source: The authors (2024).

The waste consumption in the produced composites was notably high. When considering the volume of dry materials, including binders and aggregates, 80 to 90% of the composite volume comprised waste. At 28 days, the compressive strength varied between 24.4 MPa and 54.6 MPa, while the flexural strength ranged from 6.5 MPa to 11.7 MPa.

According to Mehta and Monteiro (Mehta; Monteiro, 2006), high-performance concrete possesses at least one distinctive characteristic not found in conventional cementitious materials. These characteristics may include: (i) high constructability, (ii) increased productivity through heightened durability, (iii) high ultimate strength coupled with moderate initial strength, (iv) environmental friendliness, achieved by maximizing the incorporation of industrial by-products, and (v) cost-effectiveness. Considering the composition of the developed mixtures and the obtained mechanical results, it can be

asserted that high-performance composites were successfully produced. This achievement can be attributed to: (i) a particle packing strategy (Franco de Carvalho et al., 2019, 2020), (ii) the quality of the slag aggregate utilized, featuring high mechanical strength and suitable angularity (Geiseler, 1996; Qasrawi, 2014), and (iii) the use of NFCs to enhance the overall quality of the composite (Goncalves et al., 2019; Mejdoub et al., 2016; Onuaguluchi; Panesar; Sain, 2014).

4.4. CONCLUSIONS AND FUTURE PERSPECTIVES

In this study, eco-efficient cementitious composites were created with a significant inclusion of steel slag and NFCs. The compressive strength, flexural strength, microstructure and eco-efficiency of mortars with different contents of NFCs and BOFS were investigated by the first time. The key conclusions drawn from the research are as follows:

- i. Achieving a higher packing factor in cementitious composites enhances mechanical performance. However, this improvement is accompanied by reduced workability, necessitating the use of substantial superplasticizer contents. The inclusion of fibers also negatively impacts workability. Based on the results, incorporating NFCs up to 0.2%, along with packing factors up to 0.72, produces specimens with both good mechanical performance and workability.
- ii. Samples containing slag powder and NFC exhibit a tendency to stabilize their strength between 28 and 56 days, contrasting with specimens lacking BOFS powder, which demonstrate a notable strength increase. Notably, the inclusion of 0.2% NFC enhances the flexural strength gain from 7 to 28 days.
- iii. The higher the inclusion of BOFS powder, the lower the mechanical strength of the composites. However, this decrease in mechanical strength is offset by an increase in eco-efficiency, as the reduction in cement consumption outweighs the impact on strength. Conversely, the addition of fibers contributes to an enhancement in flexural strength and overall eco-efficiency.

- iv. Through the synergy of particle packing strategies, the use of steel slag as aggregate and supplementary cementing material, and the incorporation of NFC, the production of high-performance cementitious composites was achieved. These composites boast significant residue incorporation (up to 90% by volume of dry material) and exhibit remarkable strength levels (up to 60 MPa in compression and 11.70 MPa in bending).
- v. The central composite face-centered design was an efficient strategy to prove the successful utilization of unbleached NFC in the production of cementitious composites, demonstrating the feasibility of using an NFC without the need for extra chemical treatment (bleaching).

Further research is recommended to maximize the eco-efficiency of steel slag and NFC cementitious materials. To achieve this, the following suggestions are proposed:

- i. Explore the incorporation of new materials and residues, reduce the water/cement ratio, and enhance densification to improve eco-efficiency.
- ii. Investigate the addition of higher NFC contents to achieve even greater gains in flexural strength and enhancements in compressive strength.
- iii. Examine the effect of slag powder on the structure of NFCs, verifying whether the residue can contribute to a reduction in the evolution of mechanical strength between 28 and 56 days in mixtures containing fibers.

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CHAPTER 5: BEHAVIOR OF CEMENTITIOUS MATERIALS WITH STEEL SLAG AND ADDITION OF NANOFIBRILLATED CELLULOSE EXPOSED TO HIGH TEMPERATURES

Abstract: *Efforts to create sustainable cement-based materials involve substituting natural aggregates and cement with waste materials, aiming to reduce energy consumption, CO₂ emissions, and natural resource depletion. This study investigates the performance of cementitious blends containing steel slag (SS) aggregates and partial cement replacement with SS powder at temperatures ranging from room temperature to 600 °C. Six mixtures were tested at each temperature, varying the cement replacement percentage and including nanofibrillated cellulose (NFC). Results indicate that both temperature and powder addition generally decrease mechanical strength, but using 25% powder minimizes these strength losses due to increased matrix porosity. While NFC enhances mechanical strength at room temperature, its effectiveness diminishes at higher temperatures due to increased stiffness resulting in greater vulnerability to thermal stresses. Despite these challenges, the study demonstrates the potential of cementitious composites with significant waste content for construction applications, showing satisfactory performance even at temperatures up to 600 °C.*

Keywords: Steel slag, nanofibrillated celluloses, cement-based composites, mechanical performance, high temperatures, civil construction.

5.1. INTRODUCTION

Fire poses a significant threat to civil constructions, resulting in both material losses and loss of human life. Different materials behave in distinct ways to fire, typically losing their strength and stability as temperatures rise. Due to the inherent danger, it's imperative that structures do not collapse prematurely when subjected to fire (Buchanan; Abu, 2017).

Concrete is a widely used material in civil construction, and its response to fire is well-documented and regulated by standards such as ABNT NBR 15200 (ABNT, 2012), EN 1992-1-2 (European Committee for Standardization, 2023), and ACI/TMS 216.1M (ACI, 2004). However, the environmental impact of concrete is a subject of debate due

to its primary components, notably cement and aggregates. Cement production is energy-intensive and a major source of CO₂ emissions (Nidheesh; Kumar, 2019). On the other hand, aggregates constitute a significant portion of concrete (at least three-quarters by volume) (Cree; Green; Noumowé, 2013; Neville, 2011), leading to substantial depletion of natural resources. Consequently, there has been considerable research aimed at substituting cement and aggregates with waste materials from various industries (Collivignarelli et al., 2021; Mohanta; Murmu, 2022; Rifa et al., 2023). One such waste material is steel slag (SS), a byproduct of steel manufacturing that can serve as both an aggregate and a cementitious material (Franco de Carvalho et al., 2020; Guo et al., 2019; Lai et al., 2021; Qiang; Mengxiao; Jun, 2016; Singh; Roy; Singh, 2022). However, studies investigating the behavior of concrete containing steel slag after exposure to fire are limited and relatively recent. Therefore, there is a growing need for a deeper understanding of its properties and performance at elevated temperatures, which would facilitate its utilization and standardization in fire-related scenarios.

Some works have investigated the viability of substituting natural aggregates with slag aggregates in terms of performance at high temperatures. Huang et al. (2023) conducted an evaluation on concretes with 50% and 100% replacement of natural coarse aggregate by steel slag aggregate at varying temperatures: room temperature, 400 °C, 600 °C, 800 °C, and 1000 °C. The results indicated improvements in compressive strength with total replacement, showing increases of +27.18%, +1.16%, +34.24%, +15.24%, and -14.54%, respectively, without the addition of GGBFS (ground granulated blast furnace slag). The enhanced mechanical performance of mixtures with SS aggregates was attributed to the higher wet packing density achieved, the cementing properties of the aggregate, and the improved interaction between the cement paste and aggregates due to the more angular shape. Lai et al. (2023) investigated the complete replacement of natural coarse aggregates with basic oxygen furnace slag (BOFS) across the same temperature ranges as Huang et al. (2023). They observed increases in compressive strength of +21.87%, +26.05%, +33.90%, +36.67%, and +25% at room temperature, 400 °C, 600 °C, 800 °C, and 1000 °C, respectively. Both studies also utilized supplementary cementitious materials (SCM) such as GGBFS (Huang et al., 2023) and fly ash (FA) (Lai et al., 2023), which contributed to the enhanced performance of the samples.

Liu et al. (2022) examined the potential of using steel slag (SS) as a substitute for calcium aluminate cement (CAC) to enhance the high-temperature performance of

cement pastes designed for refractory applications. They conducted experiments replacing varying proportions of CAC with SS: 30%, 40%, 50%, and 60%. Remarkably, the replacement of 40% of CAC with SS, which passed through a 600-mesh sieve, produced the most promising outcome. When subjected to 800 °C after 14 days of curing, this particular formulation exhibited no loss of mechanical strength. Ho et al. (2024) investigated the incorporation of steel slag (SS) as a substitute for ordinary Portland cement (OPC) in concrete. They utilized two fractions of steel slag: a finer fraction with a particle size of 75 µm, termed fine steel slag (FSS), and a coarser fraction with particles of 150 µm, referred to as coarse steel slag (CSS). Additionally, natural fine and coarse aggregates were employed. The substitutions for SS were set at 10%, aiming to assess the performance of samples exposed to temperatures ranging from 200 °C to 800 °C. At initial temperatures, mixtures containing FSS exhibited higher compressive strength. In XRD, higher amounts of calcium hydroxide were found in these mixtures when compared to the control. As $\text{Ca}(\text{OH})_2$ is formed by the hydration of silicates, the higher strength can be attributed to greater hydration of mixtures with FSS. Despite the control samples experiencing less strength loss, those with FSS demonstrated greater strength up to 600 °C. Conversely, mixtures containing CSS displayed lower strength losses compared to those with FSS, attributable to a denser and more homogeneous matrix microstructure.

Another approach to enhancing the post-fire performance of cementitious composites involves incorporating both artificial and natural fibers. Afzal e Khushnood (2021) investigated the effects of incorporating carbon nanofibers (up to 0.2%) into concrete exposed to temperatures of up to 800 °C. The high thermal conductivity of these fibers facilitated improved distribution of thermal stress. Moreover, by maintaining stability up to the maximum tested temperature, they functioned through a bridge effect mechanism, controlling crack propagation and enhancing load transfer under tension within the matrix. Liu e Tan (2018) examined the effectiveness of PVA fibers in reducing spalling in cementitious composites subjected to temperatures up to 300 °C. Since the melting point of the fibers was 240 °C, voids were observed in the interfacial transition zone (ITZ) surrounding the fibers, along with holes at the fiber ends. These features augmented the permeability of the matrix and enhanced its resistance against spalling, due to the relief of vapor pressures through the pores formed. Zhang et al. (2020) explored the utilization of jute fibers as a substitute for synthetic PVA fibers. Their investigation involved assessing the performance of concrete specimens exposed to temperatures up to 800 °C. It was observed that as the temperature increased, the jute fibers underwent

shrinkage, leading to the creation of interfacial spaces within the matrix. This phenomenon resulted in increased permeability of the matrix, ultimately aiding in the control of spalling. Zhang, Tan e Tan (2021) combined steel fibers with flax fibers to enhance the performance of ultra-high-performance concrete under high temperatures, evaluating temperatures ranging from 30 °C to 800 °C. A synergistic effect between the two types of fibers was observed, effectively preventing spalling. As the temperature increased, flax fibers underwent shrinkage, creating interfacial gaps, while steel fibers expanded, generating microcracks. This mechanism resulted in the formation of interconnected channels within the matrix, increasing its permeability and mitigating spalling. Additionally, the steel fibers contributed through a bridging effect, restraining the propagation of cracks with increasing temperature.

Although studies have explored the use of natural fibers to enhance concrete performance at elevated temperatures, research on nanofibrillated cellulose (NFC) in this regard remains limited. The sole study identified during the literature review was conducted by Hoyos et al. (2019), who evaluated temperatures up to 250 °C. Prior to fiber degradation at this temperature, NFC effectively minimized the formation of microcracks within the matrix. Consequently, further investigation into NFC is needed, particularly focusing on temperatures exceeding 300 °C.

In light of the aforementioned considerations, the present study aims to assess the post-fire behavior of cementitious composites incorporating Basic Oxygen Furnace Slag (BOFS) aggregates, BOFS powder as a supplementary cementitious material, and nanofibrillated cellulose (NFC). Temperatures of 200 °C, 400 °C, and 600 °C are examined, with the objective of addressing some gaps in the existing literature. Notably, no studies were found that utilize 100% BOFS aggregates in combination with BOFS powder as a partial substitute for cement in high-temperature scenarios. Additionally, this study conducts an initial and unprecedented investigation into the impact of NFCs under these conditions. A factorial design approach has been adopted to better understand the influence and significance of each of the factors being evaluated.

5.2. MATERIALS AND METHODS

5.2.1. Materials

BOFS from Arcelor-Mittal Company served as the primary material for aggregate and SCM production. This material was stored and exposed to weather conditions for five years in the courtyard of the Laboratory of Civil Construction Materials at the Federal University of Ouro Preto - UFOP, located in the state of Minas Gerais, Brazil.

Initially, the material underwent processing in Los Angeles equipment for 40 minutes and was subsequently sieved, following the procedure outlined in Chapter 3. The portion that passed through the sieve with an opening of 2.36 mm was separated and utilized as aggregate. The remaining material was then subjected to further processing in the Los Angeles equipment for 120 minutes and sieved again, as per Chapter 4. The fraction passing through the sieve with an opening of 0.15 mm (referred to as powder) was employed as a partial substitute for cement in certain mixtures.

The unbleached nanofibrillated cellulose was obtained from Pinus and produced through a delamination process. This material was supplied by Embrapa Florestas, located in Colombo, Paraná, Brazil.

This study employed high early strength Portland cement (CPV-ARI), equivalent to ASTM Type III cement. To prepare the specimens, a polycarboxylate-based superplasticizer (MC-PowerFlow 4001) was utilized. This superplasticizer was chosen to enhance the workability of the mixtures and reduce the required water-cement ratio.

5.2.2. Factorial design of experiment

The aim was to assess the impact of three factors on the mechanical properties of cementitious composites: temperature, powder/cement content, and NFC content. To achieve this, a 4 x 3 x 2 factorial design was employed, encompassing four levels for the temperature factor (25 °C, 200 °C, 400 °C, and 600 °C), three levels for the powder/cement volume ratio (0%, 25%, and 50%), and two levels (0% and 0.2%) of NFC content by mass in relation to cement in the reference mixture.

Table 1 outlines the proportions of materials used in each mixture. The quantity of SP was adjusted to maintain consistent workability across all mixtures. This adjustment ensured that the compaction process would not introduce variations that could affect the results.

Table 1 - Mass ratio of mixtures.

Mixture	Cement	BOFS powder	BOFS aggregate	SP	Water	NFC
R-0	1	0.0	4.6	0.008	0.63	0.0
0.2-0	1	0.0	4.6	0.030	0.61	0.002
R-25	0.8	0.3	4.6	0.008	0.63	0.0
0.2-25	0.8	0.3	4.6	0.028	0.61	0.002
R-50	0.5	0.6	4.6	0.006	0.6	0.0
0.2-50	0.5	0.6	4.6	0.025	0.6	0.002

* The first part of the mixture name refers to the NFC content (R when there is no NFC and 0.2 when 0.2% NFC is used). The second part refers to the cement content replaced by BOFS powder in volume (0%, 25%, and 50%).

Source: The author (2024).

The variables investigated included compressive strength, flexural strength, and dynamic modulus of elasticity, along with their respective residual factors.

5.2.3. Production of cementitious composites

The test specimens were fabricated following the methodology outlined in Chapter 4. Initially, cement, BOFS aggregate, and powder (if applicable) were pre-mixed and set aside. For mixtures containing NFC, the required amount of water and NFC underwent sonication using a 50 W probe sonicator operating at a frequency of 20 kHz for a duration of 0.04 min/ml. Subsequently, SP was introduced into the solution (or into water for mixtures without NFC) and stirred for 30 seconds.

In the subsequent step, the dry materials were added to a mixer containing water or NFC solution while stirring continued for 10 minutes. Following this period, with all constituents incorporated, the mixture underwent an additional 5 minutes of stirring to ensure complete homogenization.

Following this procedure, prismatic specimens measuring 2 cm x 2 cm x 8 cm were molded for mechanical testing. Additionally, cylindrical specimens with a diameter of 2 cm and a height of 6 cm were molded for the purpose of monitoring the temperature within the furnace chamber. Compaction was executed on a vibrating table in two layers, with each layer subjected to vibration for 15 seconds.

Subsequently, the specimens were transferred to a humid chamber for curing, where they remained for 28 days at a controlled temperature of 23 ± 2 °C and humidity of 95% (Figure 1).

Figure 1 - Specimens being cured in the humid chamber.



Source: The author (2024).

5.2.4. Characterization of behavior after fire

After the 28-day curing period, the specimens were removed from the humid chamber and subjected to drying at 60 °C for 48 hours. This drying step was conducted to prevent the abrupt occurrence of spalling, a phenomenon slated for evaluation in future research endeavors. Following the 48-hour drying period, specimens designated for non-heating tests were allowed to slowly cool to 25 °C before testing.

For other test specimens, exposure to temperatures of 200 °C, 400 °C, and 600 °C was initiated. Heating was performed using a furnace chamber, specifically the Linn Elektro Therm model, with an average heating rate of 10 °C/min. Temperature monitoring during heating was conducted via three type K thermocouples. One thermocouple monitored the internal temperature of the furnace chamber (TF), while the second was coupled to a cylindrical specimen derived from the mixture without powder and NFC, facilitating the monitoring of temperature within this sample (TR). The third thermocouple was associated with a specimen from the mixture containing the maximum amount of powder and NFC, enabling temperature monitoring at its core (TM).

Data acquisition was carried out using a National Instruments (NI) data acquisition system with an NI-9219 module, employing an application developed in Labview, in accordance with the methodology outlined by Nalon et al. (2021). The assembly setup is depicted in Figure 2.

Once the specimens monitored by the thermocouples reached the target temperatures of 200 °C, 400 °C, or 600 °C, the temperature was maintained constant for

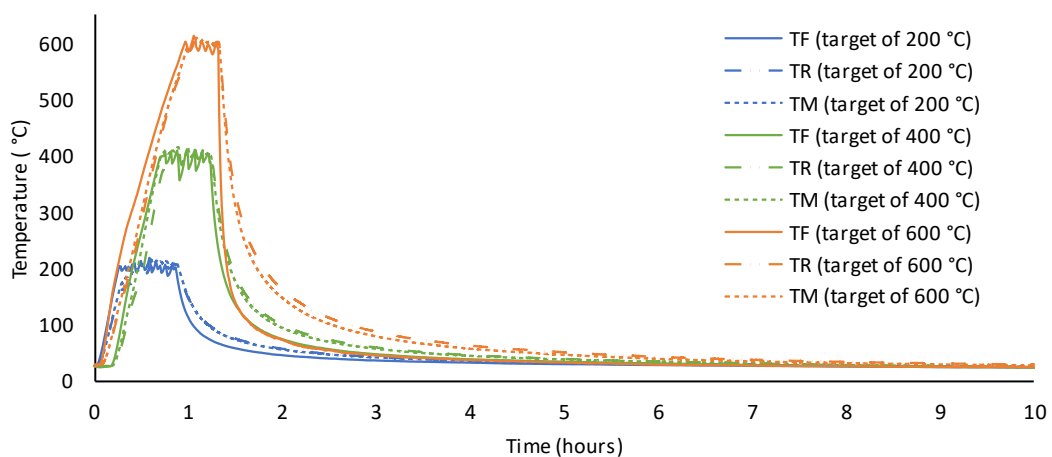
a duration of 15 minutes, in order to homogenize the test specimens temperature. Subsequently, the furnace chamber was switched off, and the specimens were left inside, allowing them to cool gradually (Figure 3).

Figure 2 - Experimental setup for the thermal treatments.



Source: The author (2024).

Figure 3 - Heating and cooling curve of the specimens.



Source: The author (2024).

Following the gradual cooling process, four specimens from each mixture were selected for the dynamic modulus of elasticity test, conducted in accordance with ABNT NBR 15630:2008 (ABNT, 2008) (corresponding to ASTM C597-22 (ASTM, 2022)).

These same specimens were subsequently employed for the flexural strength test, following the method ABNT NBR 13279:2005 (ABNT, 2005) (test corresponding to ASTM C348-21 (ASTM, 2021)). Additionally, the two halves resulting from the flexural test were utilized for the compressive strength test, also following the method ABNT NBR 13279:2005 (ABNT, 2005) (test corresponding to ASTM C349-18 (ASTM, 2018)).

Using the obtained results, the relative factors of residual mechanical properties (Φ_j) were computed, as per the methodology outlined by Nalon et al. (2021). These factors represent the ratio between the value of the residual mechanical property after exposure to high temperature (k_j^{res}) and the average mechanical property of specimens from the same mixture that were not subjected to high temperatures ($k_m^{25^\circ\text{C}}$), as described in Eq. (1). Relative factors for compressive strength, flexural strength, and dynamic modulus of elasticity were determined through this calculation process.

$$\Phi_j = \frac{k_j^{res}}{k_m^{25^\circ\text{C}}} \quad (1)$$

5.3. RESULTS AND DISCUSSION

To facilitate a comprehensive understanding of the results, the performance of the mixtures at each analyzed temperature will be discussed initially. Following this, the factor analysis will be addressed, taking into account the influence of temperature, NFC, and powder content concurrently.

5.3.1. Room temperature

Figure 4 illustrates the mechanical results of the tested mixtures at room temperature. Observing mixtures with equivalent cement replacement content by powder, the addition of NFC yields enhancements in mechanical strength and dynamic modulus. This improvement is particularly notable in mixtures devoid of powder, manifesting as a 27.42% increase in compressive strength, a 21.38% increase in flexural strength, and a 22.90% increase in dynamic modulus of elasticity. Statistical analysis using the Tukey test confirms the significance of these differences (Table 2). These findings align with existing literature and can be attributed to various mechanisms of NFCs within the cement

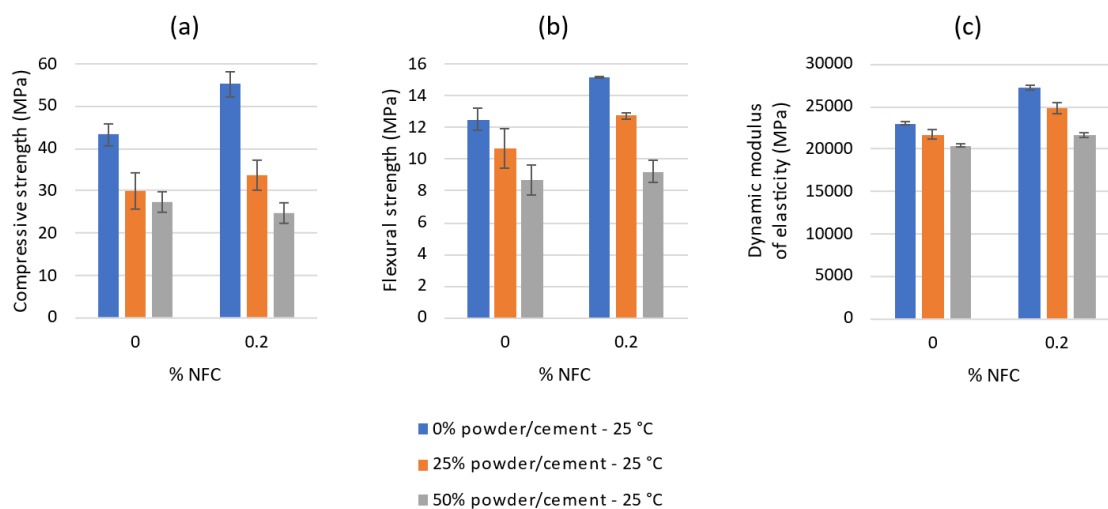
matrix, including the bridging effect, matrix refinement as a nucleation point, and the short circuit effect (Hoyos et al., 2019; Mejdoub et al., 2016; Santos et al., 2021).

For a cement replacement content of 25% with BOFS powder, the enhancements were observed as follows: a 12.7% increase in compressive strength, a 19.31% increase in flexural strength, and an 11.93% increase in dynamic modulus of elasticity. However, in this scenario, the increase was statistically not significant only for compressive strength.

Conversely, for a cement replacement content of 50% with BOFS powder, there was a 9.90% reduction in compressive strength, a 6.32% increase in flexural strength, and a 7.75% increase in dynamic modulus of elasticity. According to the Tukey test, only the increase in dynamic modulus of elasticity was statistically significant.

In general, a trend is observed wherein the higher the replacement of cement with powder, the lower the mechanical strength of the samples. This phenomenon may arise from the fact that SS powder possesses inferior hydraulic activity compared to cement, owing to its reduced quantity of hydraulic components. Consequently, the matrix tends to exhibit greater porosity (Martins et al., 2021).

Figure 4 - Results of the mechanical properties of the mixtures at room temperature: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.



Source: The author (2024).

Table 2 - Tukey test for the mechanical properties of mixtures at room temperature: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.

(a)				(b)			
Compressive strength (MPa)				Flexural strength (MPa)			
Mixture	N	Mean	Grouping	Mixture	N	Mean	Grouping
2-0-25	8	55.22	A	2-0-25	3	15.20	A
R-0-25	8	43.34	B	2-25-25	3	12.75	B
2-25-25	8	33.63	C	R-0-25	4	12.52	B C
R-25-25	8	29.98	C D	R-25-25	4	10.68	C D
R-50-25	8	27.46	D E	2-50-25	4	9.24	D E
2-50-25	7	24.75	E	R-50-25	4	8.69	E

(c)			
Dynamic modulus (MPa)			
Mixture	N	Mean	Grouping
2-0-25	4	27232	A
2-25-25	4	24851	B
R-25-25	4	22202	C
R-0-25	3	22159	C
2-50-25	4	21843	C
R-50-25	4	20272	D

Source: The author (2024).

5.3.2. Temperature of 200 °C

Figure 5 depicts the mechanical results of the mixtures subjected to heating at 200 °C. The inclusion of NFC leads to improvements in compressive strength and dynamic modulus for equivalent cement replacement content with powder. This enhancement is particularly notable in mixtures lacking powder, with an increase of 16.70% in compressive strength and 7.76% in dynamic modulus of elasticity. All these differences were statistically significant based on the Tukey test (Table 3).

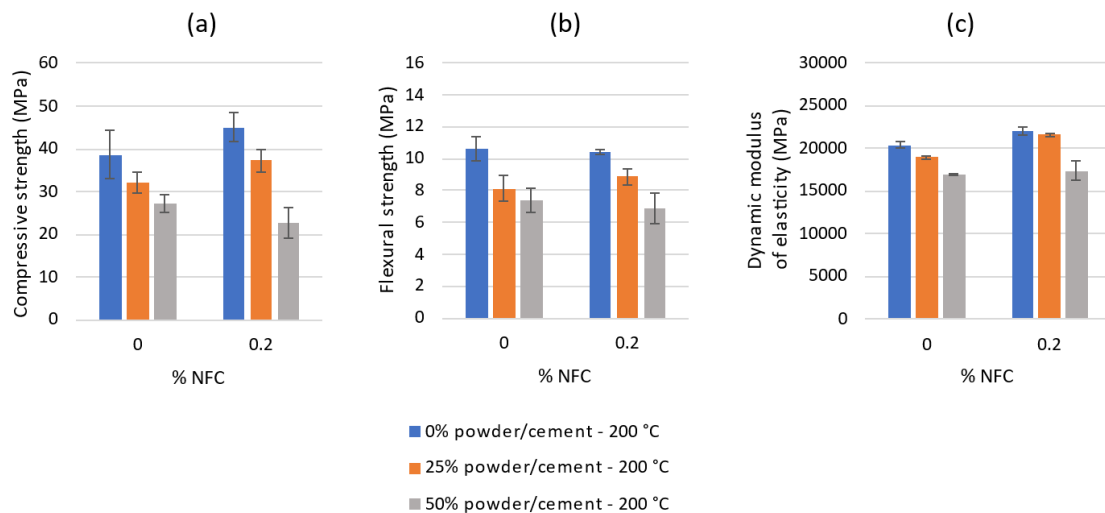
For a cement replacement content of 25% with BOFS powder, increases of 15.63% in compressive strength and 12.37% in dynamic modulus of elasticity were observed. In this case, the increase was statistically not significant only for compressive strength.

Finally, for a cement replacement content of 50% with BOFS powder, there was a reduction of 16.51% in compressive strength and an increase of 8.19% in dynamic modulus of elasticity. According to the Tukey test, only the increase in dynamic modulus of elasticity was statistically significant.

These findings suggest that fibers have a positive impact on mixtures containing up to 25% powder when exposed to 200 °C, consistent with observations made during tests at room temperature. This behavior aligns with the findings of Hoyos et al. (2019), who noted that NFCs can mitigate microcrack formation up to 250 °C.

As for flexural strength, no statistically significant difference was observed. However, for mixtures with 0% powder and 50% powder contents, there is a tendency for a reduction in strength of -2.46% and -6.83%, respectively, when NFC is added. In contrast, for mixtures with a 25% powder content, there is a tendency for strength to increase by 8.89%. When considering the use of BOFS powder, it is noted that the higher the cement replacement with powder, the lower the mechanical strength of the samples, similar to observations at room temperature.

Figure 5 - Results of the mechanical properties of the mixtures at 200 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.



Source: The author (2024).

Table 3 - Tukey test for the mechanical properties of mixtures at 200 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.

(a)				(b)			
Compressive strength (MPa)				Flexural strength (MPa)			
Mixture	N	Mean	Grouping	Mixture	N	Mean	Grouping
2-0-200	8	45.08	A	R-0-200	4	10.64	A
R-0-200	8	38.63	B	2-0-200	4	10.37	A B
2-25-200	8	37.31	B C	2-25-200	4	8.87	B C
R-25-200	8	32.27	C D	R-25-200	4	8.14	C D
R-50-200	8	27.18	D E	R-50-200	4	7.40	C D
2-50-200	8	22.69	E	2-50-200	4	6.89	D

(c)			
Dynamic modulus (MPa)			
Mixture	N	Mean	Grouping
2-0-200	4	21964	A
2-25-200	4	21394	A B
R-0-200	4	20382	B
R-25-200	4	19039	C
2-50-200	4	18490	C
R-50-200	3	17091	D

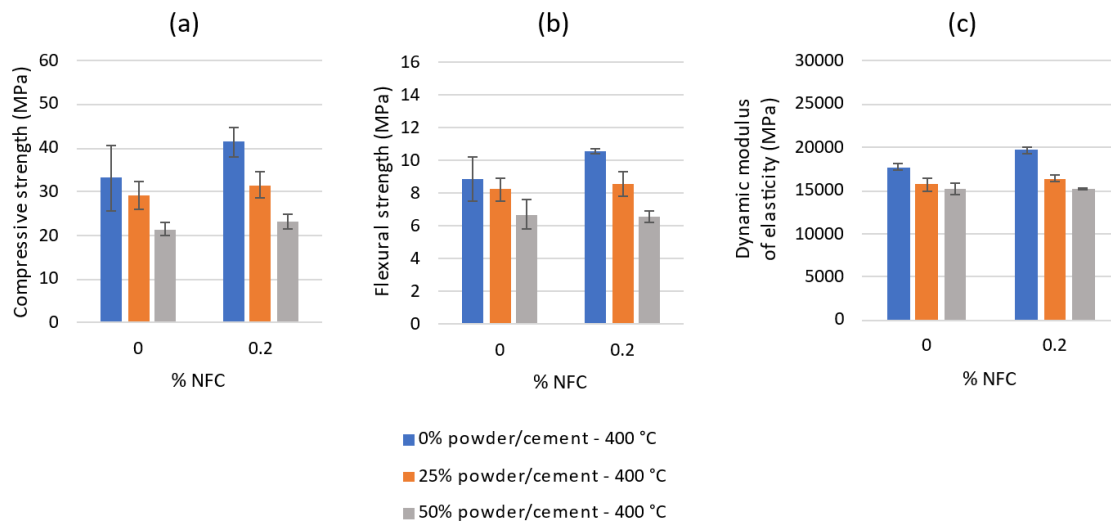
Source: The author (2024).

5.3.3. Temperature of 400 °C

Figure 6 displays the mechanical results of the mixtures exposed to heating at 400 °C. Notably, for equivalent cement replacement content with powder, the addition of NFC leads to substantial gains only in compressive strength when no powder is added. This enhancement amounts to 24.80%. In the other cases, the differences were not statistically significant according to the Tukey test (Table 4). However, mixtures containing NFC tend to exhibit higher values for strength and modulus of elasticity.

Concerning the powder content, a consistent trend is observed: the higher the cement replacement with powder, the lower the mechanical strength of the samples. This pattern aligns with observations made at previous temperatures.

Figure 6 - Results of the mechanical properties of the mixtures at 400 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.



Source: The author (2024).

Table 4 - Tukey test for the mechanical properties of mixtures at 400 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.

(a)				(b)			
Compressive strength (MPa)				Flexural strength (MPa)			
Mixture	N	Mean	Grouping	Mixture	N	Mean	Grouping
2-0-400	8	41.41	A	2-0-400	4	10.56	A
R-0-400	8	33.18	B	R-0-400	4	8.90	A B
2-25-400	8	31.50	B	2-25-400	4	8.58	B
R-25-400	8	29.05	B C	R-25-400	4	8.27	B C
2-50-400	8	23.31	C D	R-50-400	4	6.70	C
R-50-400	8	21.45	D	2-50-400	4	6.60	C

(c)			
Dynamic modulus (MPa)			
Mixture	N	Mean	Grouping
2-0-400	4	19529	A
R-0-400	4	17709	B
2-25-400	4	16771	B C
R-25-400	4	16240	C D
2-50-400	3	15500	D E
R-50-400	4	14716	E

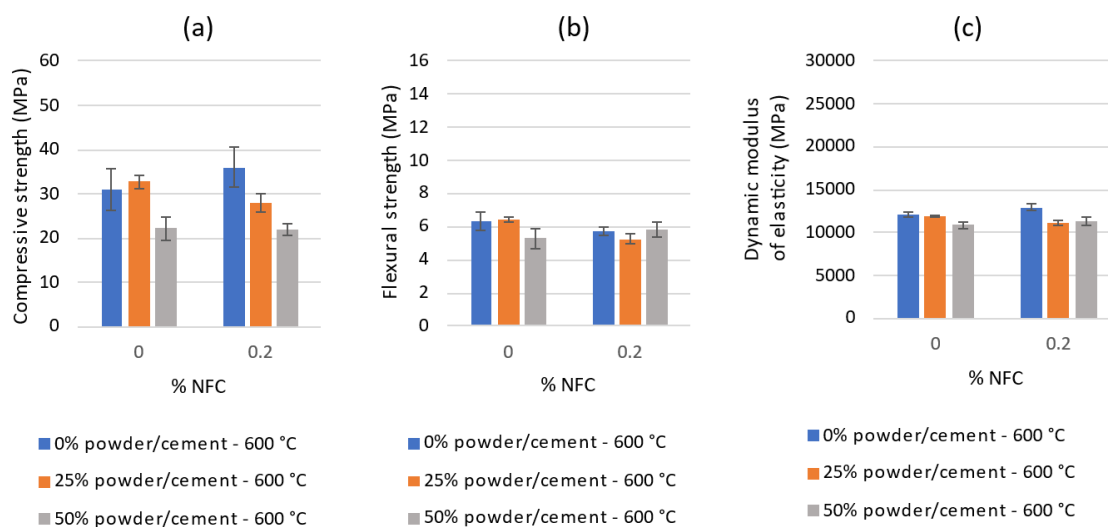
Source: The author (2024).

5.3.4. Temperature of 600 °C

Figure 7 presents the mechanical results of the mixtures subjected to heating at 600 °C. For the most part, no statistically significant differences were observed within the same powder content (Table 5). However, exceptions were noted for mixtures with 0% powder, where NFC led to a gain of 16.25% in compressive strength and 7.39% in dynamic modulus. Additionally, for mixtures with 25% powder, there was a reduction of 14.53% in compressive strength and 17.95% in flexural strength. Furthermore, it is noteworthy that, except for compressive strength, the degree of cement replaced by powder has less influence on mechanical properties.

Between 400 °C and 600 °C, a series of detrimental events occur that negatively impact the performance of cementitious materials. These include the intensification of microcracks due to the decomposition of portlandite, dehydration reactions, and thermal stress, as documented in Nalon et al. (2021). In light of these occurrences, it is evident that the results obtained at 600 °C are inferior to those observed at 400 °C.

Figure 7 - Results of the mechanical properties of the mixtures at 600 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.



Source: The author (2024).

Table 5 - Tukey test for the mechanical properties of mixtures at 600 °C: (a) compressive strength; (b) flexural strength; (c) dynamic modulus of elasticity.

(a)				(b)			
Compressive strength (MPa)				Flexural strength (MPa)			
Mixture	N	Mean	Grouping	Mixture	N	Mean	Grouping
2-0-600	8	36.06	A	R-25-600	4	6.42	A
R-25-600	8	32.80	A B	R-0-600	4	6.39	A
R-0-600	8	31.02	B C	2-50-600	4	5.79	A B
2-25-600	8	28.03	C	2-0-600	4	5.73	A B
R-50-600	8	22.21	D	R-50-600	4	5.29	B
2-50-600	8	22.05	D	2-25-600	4	5.27	B

(c)			
Dynamic modulus (MPa)			
Mixture	N	Mean	Grouping
2-0-600	4	12955	A
R-0-600	4	12063	B
R-25-600	3	11882	B C
2-50-600	4	11326	B C D
2-25-600	4	11182	C D
R-50-600	4	10862	D

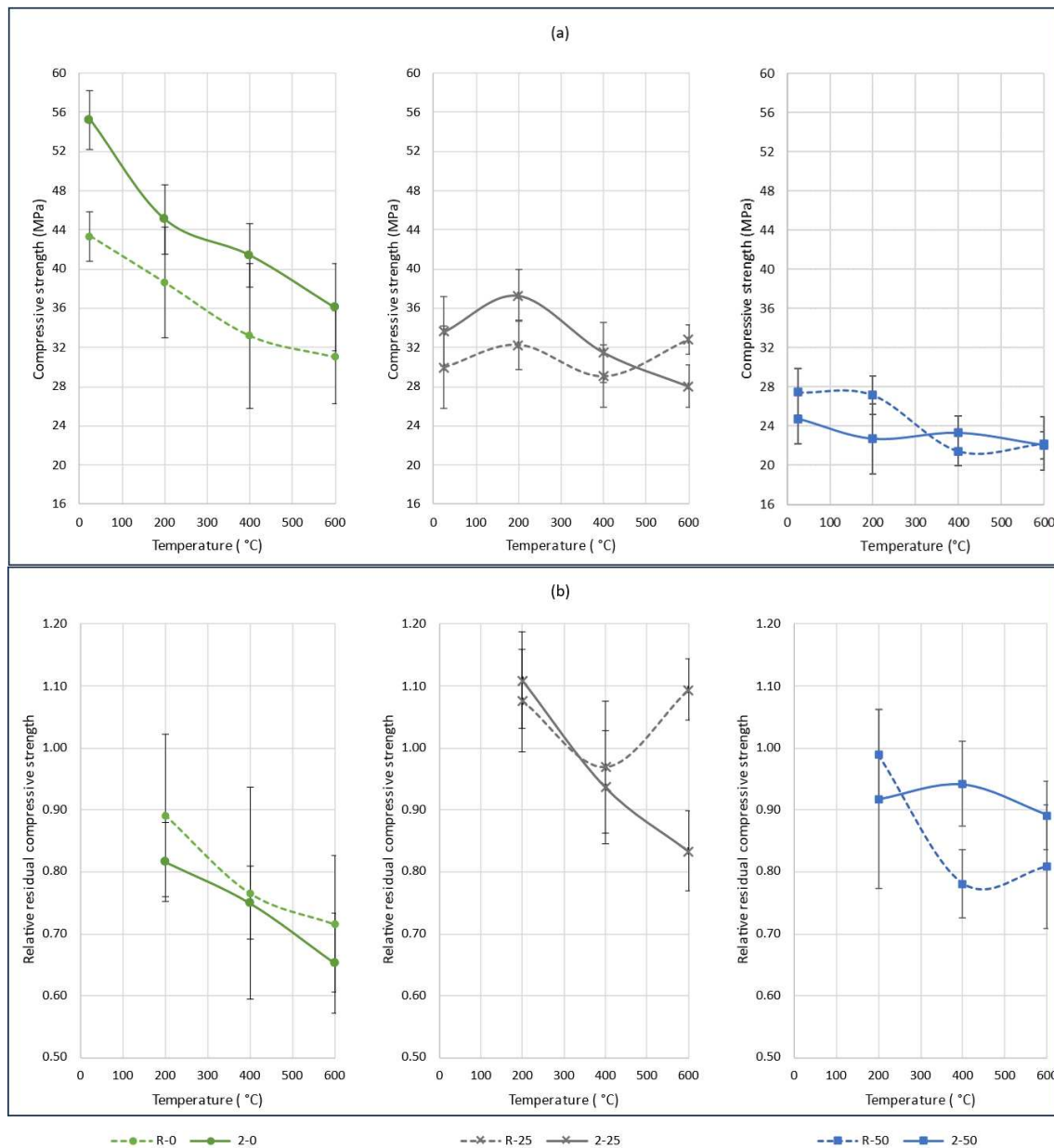
Source: The author (2024).

5.3.5. Results of factorial design

5.3.5.1. Compressive strength

Figure 8a and Table 6 display the compressive strength of the mixtures produced under varying temperature conditions. Overall, it is evident that higher powder content correlates with lower compressive strength. Furthermore, in samples without powder, compressive strength tends to decrease as temperature increases. However, the impact of temperature on compressive strength is less pronounced in samples with powder.

Figure 8 - (a) Compressive strength and (b) relative residual compressive strength factor of cementitious composites.



Source: The author (2024).

According to the Pareto chart (Figure 9), it is evident that all evaluated factors (temperature, powder content, and NFC content) are significant, with the model having a coefficient of determination (R^2) of 86.81%, indicating good data adequacy. Among the individual factors, temperature and powder content exert the greatest influence on the results. Additionally, the interaction between temperature and powder content, as well as between powder content and NFC content, also exhibits significant influence. Conversely, the isolated factor of NFC content, the interaction between temperature and

NFC content, and the interaction among all three factors have a comparatively lesser impact.

Table 6 - Tukey test for the compressive strength of mixtures.

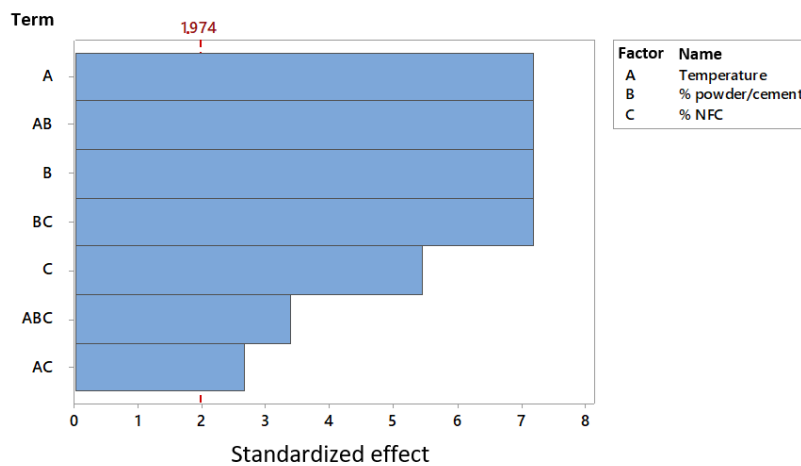
Temperature*%powder/cement *% NFC	N	Mean	Grouping
25 0 0.2	8	55.2193	A
200 0 0.2	8	45.0822	B
25 0 0.0	8	43.3367	B C
400 0 0.2	8	41.4102	B C D
200 0 0.0	8	38.6255	C D E
200 25 0.2	8	37.3134	C D E F
600 0 0.2	8	36.0637	D E F G
25 25 0.2	8	33.6303	E F G H
400 0 0.0	8	33.1847	E F G H I
600 25 0.0	8	32.7980	E F G H I
200 25 0.0	8	32.2685	F G H I
400 25 0.2	8	31.5036	F G H I
600 0 0.0	8	31.0198	F G H I J
25 25 0.0	8	29.9774	G H I J
400 25 0.0	8	29.0504	H I J K
600 25 0.2	8	28.0334	H I J K L
25 50 0.0	8	27.4635	H I J K L M
200 50 0.0	8	27.1770	I J K L M
25 50 0.2	7	24.7457	J K L M
400 50 0.2	8	23.3047	K L M
200 50 0.2	8	22.6933	L M
600 50 0.0	8	22.2119	L M
600 50 0.2	8	22.0534	L M
400 50 0.0	8	21.4462	M

Source: The author (2024).

Figure 10 illustrates that only the NFC content has a positive effect on compressive strength, indicating the beneficial use of nanofibers. This observation is corroborated by Figure 8a. Conversely, higher values of temperature and powder lead to lower compressive strengths.

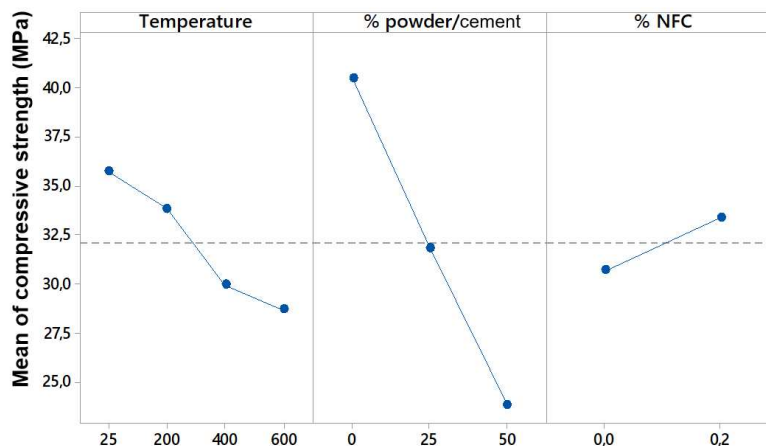
Figure 11 provides insights into the interaction between factors. It is apparent that temperature has a significant influence on mixtures without powder. However, the compressive strength varies minimally in mixtures with powder across different temperatures. This feature is particularly intriguing for products exposed to high temperatures. This phenomenon can be attributed to the greater porosity promoted by the powder in the cement matrix (Martins et al., 2021). The increased number of voids contributes to relieving thermal stresses. Conversely, denser matrices, such as mixtures without powder, are more susceptible to thermal stresses, which explains the more pronounced decrease in strength as temperature rises (Huang et al., 2023). Additionally, in mixtures with powder, cement consumption is reduced, thereby enhancing the sustainability of the product (Franco de Carvalho et al., 2021).

Figure 9 - Pareto chart to compressive strength ($\alpha = 0.05$).



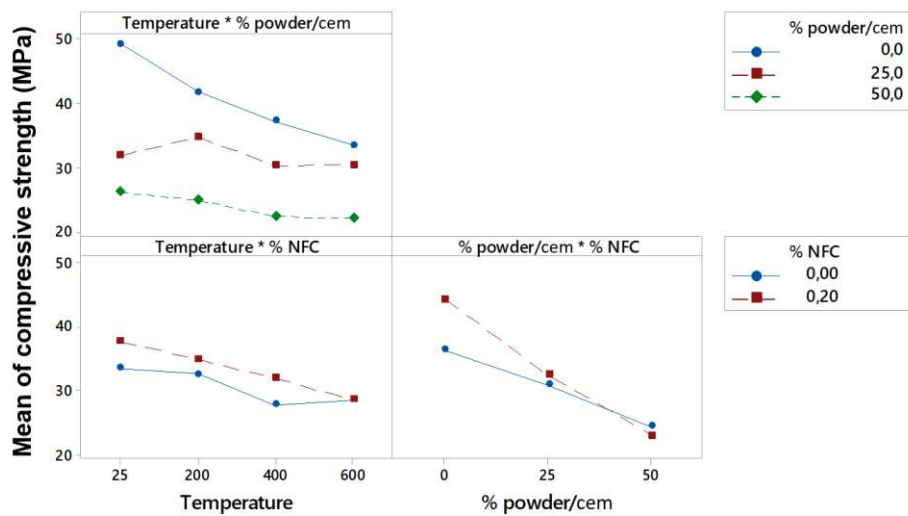
Source: The author (2024).

Figure 10 - Main Effects Plot for compressive strength (temperature in °C).



Source: The author (2024).

Figure 11 - Interaction plot for compressive strength (temperature in °C).



Source: The author (2024).

Regarding fibers, temperature exerts a more pronounced influence on the loss of strength when NFC is present in the mixtures. In cases of mixtures without powder at room temperature, NFCs exhibited markedly superior results, stemming from a denser matrix (as supported by subsequent discussions on dynamic modulus of elasticity). However, as temperature rises, this denser matrix becomes increasingly vulnerable to thermal effects. This trend persists even in the presence of fiber shrinkage and degradation.

Finally, it is observed that the powder content has a more significant impact on the reduction of compressive strength in mixtures with NFC addition. This suggests that higher amounts of powder may create an environment that interferes more with the properties of the fibers. Hence, further investigation in future studies is recommended to validate this hypothesis.

Figure 8b and Table 7 present the relative residual factors of the compressive strength of the mixtures at various temperatures. These factors represent the ratio between the compressive strength of samples exposed to elevated temperatures and the strength of samples at room temperature. Values closer to 1 indicate lower loss in strength due to higher temperatures.

Observations reveal that mixtures without powder experience the most significant reduction in strength as temperature increases. Conversely, mixtures with 25% powder content demonstrate the ability to maintain their strength between 200 °C and 600 °C.

Table 7 - Tukey test for relative residual compressive strength factor.

Temperature*%powder/cement *% NFC	N	Mean	Grouping
200 25 0.2	8	1.10952	A
600 25 0.0	8	1.09409	A B
200 25 0.0	8	1.07643	A B C
200 50 0.0	8	0.98957	A B C D
400 25 0.0	8	0.96907	A B C D E
400 50 0.2	8	0.94177	B C D E F
400 25 0.2	8	0.93676	B C D E F
200 50 0.2	8	0.91706	C D E F G
200 0 0.0	8	0.89129	D E F G H
600 50 0.2	8	0.89120	D E F G H
600 25 0.2	8	0.83358	D E F G H I
200 0 0.2	8	0.81642	E F G H I J
600 50 0.0	8	0.80878	E F G H I J
400 50 0.0	8	0.78090	F G H I J
400 0 0.0	8	0.76574	G H I J
400 0 0.2	8	0.74992	H I J
600 0 0.0	8	0.71579	I J
600 0 0.2	8	0.65310	J

Source: The author (2024).

A model was derived through factorial analysis, yielding an R^2 value of 68.05%. All factors and interactions are significant for the compression factors, except for the NFC content and the interaction between temperature and powder content (Figure 12). Figure 13 aids in understanding how isolated factors influence the model.

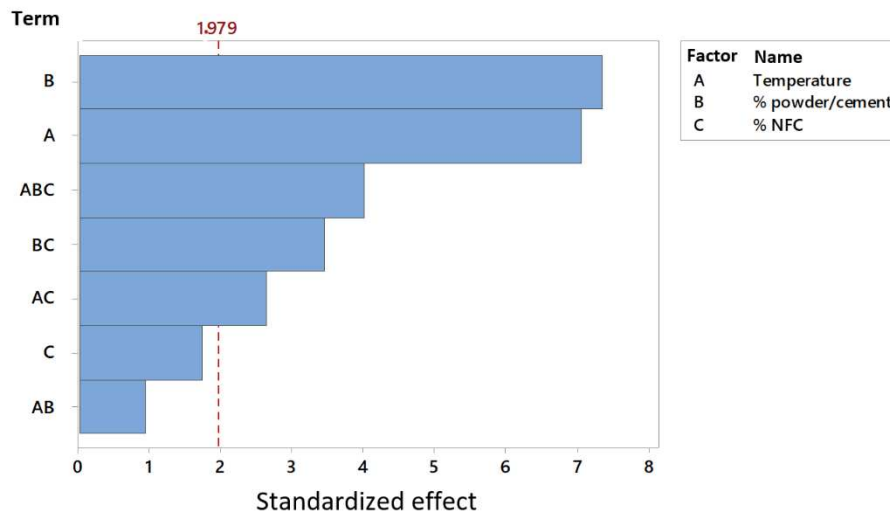
Regarding temperature, the decline in strength is most pronounced between 200 to 400 °C. This interval corresponds to the emergence of significant cracks induced by the dehydration of C-S-H (Nalon et al., 2021). From 400 to 600 °C, there is also a decrease in strength, even to a lesser extent.

The powder content positively influences the residual strength factor values up to 25%, beyond which it exerts a negative impact. While NFCs are not significant in the model, there is a tendency for fibers to lose strength at higher temperatures.

Figure 14 illustrates the interaction between different factors. Between temperature and fibers, it's apparent that mixtures containing NFC tend to experience

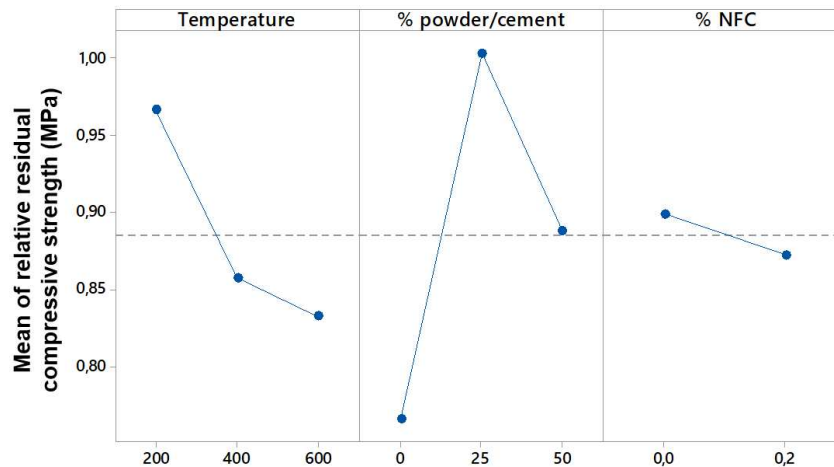
greater loss in strength, particularly at 600 °C. This outcome is associated with the denser matrix, as previously noted.

Figure 12 - Pareto chart to relative residual compressive strength ($\alpha=0.05$).



Source: The author (2024).

Figure 13 - Main Effects Plot for relative residual compressive strength factor (temperature in °C).

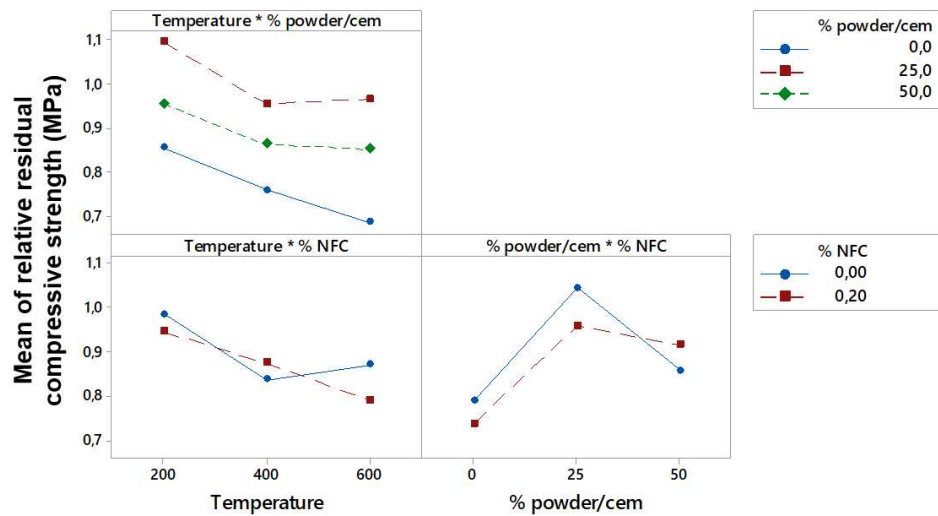


Source: The author (2024).

Regarding the relationship between powder and NFC, it is evident that with additions of up to 25% of powder, the loss of strength is lower when fibers are not present.

Although the interaction between temperature and powder was not significant, Figure 14 suggests that incorporating powder can result in reduced losses or even maintenance of compressive strength at higher temperatures.

Figure 14 - Interaction plot for relative residual compressive strength factor (temperature in °C).



Source: The author (2024).

5.3.5.2. Dynamic modulus of elasticity

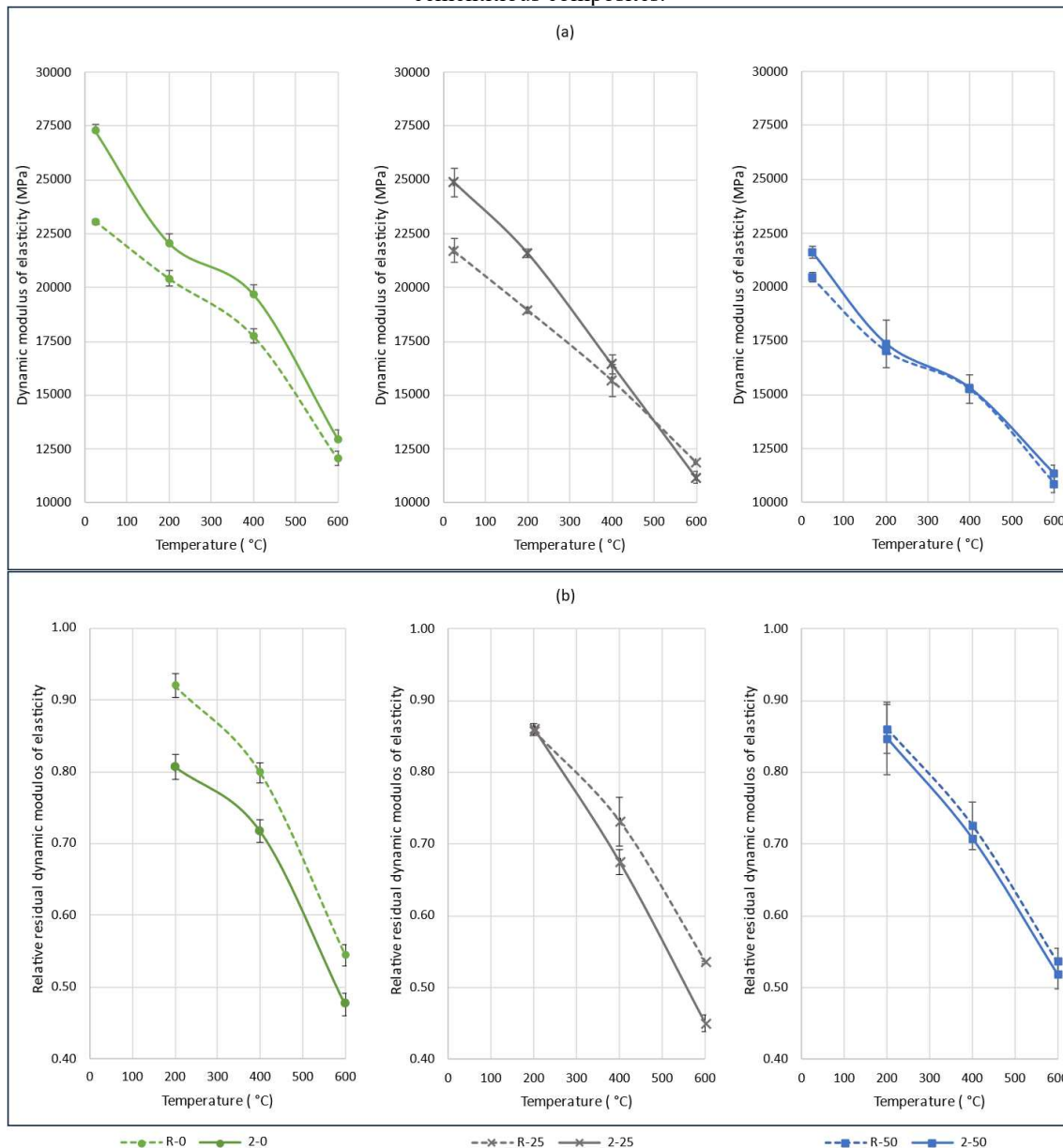
Figure 15a and Table 8 depict the dynamic modulus of elasticity of the mixtures subjected to various temperature conditions. A pattern akin to compressive strength is observed: higher powder content corresponds to lower modulus, while the presence of NFC tends to yield superior results.

Through factorial analysis, a model with R^2 equal to 99.24% was established, wherein all factors and interactions are significant (Figure 16). When examining isolated factors (Figure 17), temperature and powder content exhibit a negative impact on the modulus of elasticity, while NFC tends to positively influence the modulus.

Figure 18 displays the interaction between the three evaluated factors. Concerning temperature, the presence of NFC and the absence or lower levels of powder result in higher dynamic modulus values. Regarding powder content, nanofibers mitigate the decline in modulus values.

The consistent behavior observed in dynamic modulus of elasticity, akin to compressive strength, is attributed to a strong correlation between the two properties. This correlation is significant enough to enable the prediction of strength based on measured modulus (Wang et al., 2023). Notably, the dynamic modulus test yielded results with minimal deviations, facilitating a clearer distinction between various treatments. Consequently, this technique has proven to be suitable even for small-sized specimens.

Figure 15 - Dynamic modulus of elasticity and relative residual Dynamic modulus of elasticity factor of cementitious composites.



Source: The author (2024).

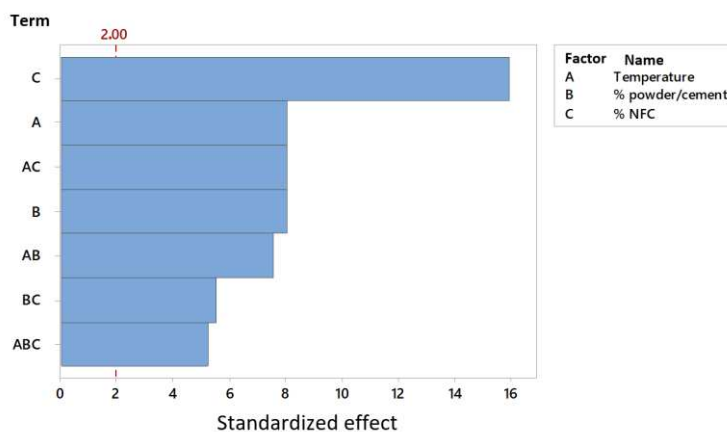
Figure 15b and Table 9 illustrate the relative residual factors of the dynamic modulus of elasticity of the mixtures at different temperatures. These factors represent the ratio between the dynamic modulus of samples exposed to higher temperatures and the modulus of samples at room temperature. A value closer to 1 indicates a smaller reduction in modulus due to higher temperatures.

Observations reveal that as the exposure temperature increases, the samples exhibit lower residual modulus. Additionally, the presence of fibers also contributes to a lower residual modulus.

Table 8 - Tukey test for the dynamic modulus of elasticity of mixtures.

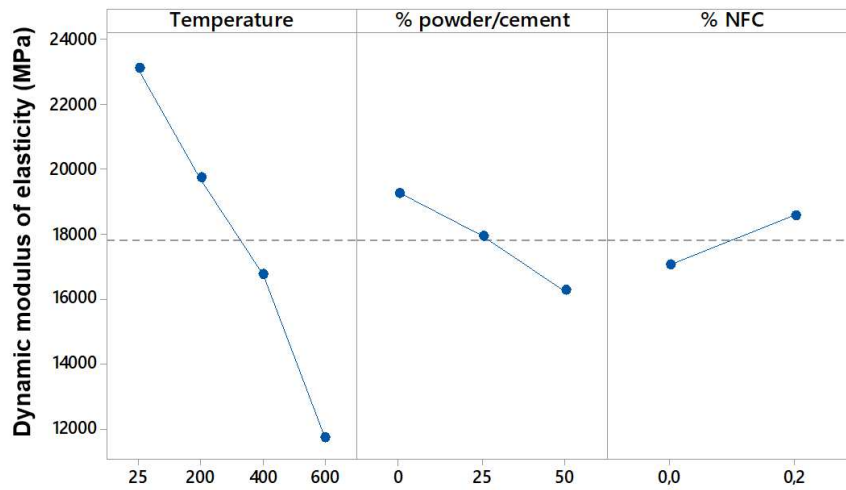
Temperature*%powder/cement *% NFC	N	Mean	Grouping
25 0 0.2	4	27231.8	A
25 25 0.2	4	24850.7	B
25 25 0.0	4	22202.2	C
25 0 0.0	3	22158.6	C
200 0 0.2	4	21964.2	C
25 50 0.2	4	21843.3	C
200 25 0.2	4	21393.5	C D
200 0 0.0	4	20382.4	D E
25 50 0.0	4	20272.0	D E
400 0 0.2	4	19529.2	E F
200 25 0.0	4	19039.1	F
200 50 0.2	4	18489.6	F G
400 0 0.0	4	17709.2	G H
200 50 0.0	3	17090.8	H I
400 25 0.2	4	16771.3	H I J
400 25 0.0	4	16239.7	I J
400 50 0.2	3	15500.0	J K
400 50 0.0	4	14716.3	K
600 0 0.2	4	12955.1	L
600 0 0.0	4	12062.9	L M
600 25 0.0	3	11882.2	L M
600 50 0.2	4	11326.1	M
600 25 0.2	4	11181.6	M
600 50 0.0	4	10862.1	M

Source: The author (2024).

Figure 16 - Pareto chart to dynamic modulus of elasticity ($\alpha=0.05$).

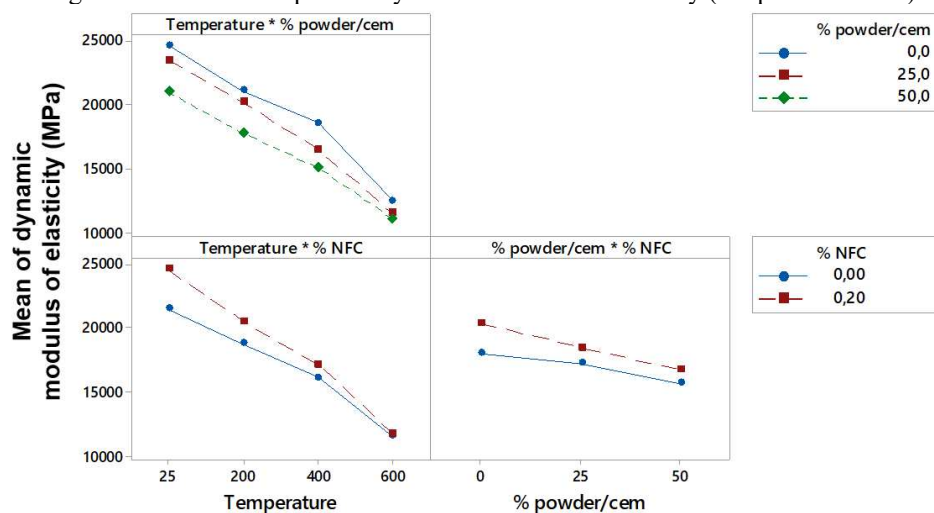
Source: The author (2024).

Figure 17 - Main Effects Plot for dynamic modulus of elasticity (temperature in °C).



Source: The author (2024).

Figure 18 - Interaction plot for dynamic modulus of elasticity (temperature in °C).



Source: The author (2024).

Factorial analysis aids in elucidating the results. A model with R^2 value of 98.52% was derived, where all factors and interactions are deemed significant, except for the interaction between temperature and NFC content (Figure 19).

Upon closer examination (Figure 20), it becomes evident that increases in temperature and the addition of NFC lead to a decrease in the residual modulus of the samples. It is highlighted that the powder content exhibits less influence compared to the temperature and the addition of NFC.

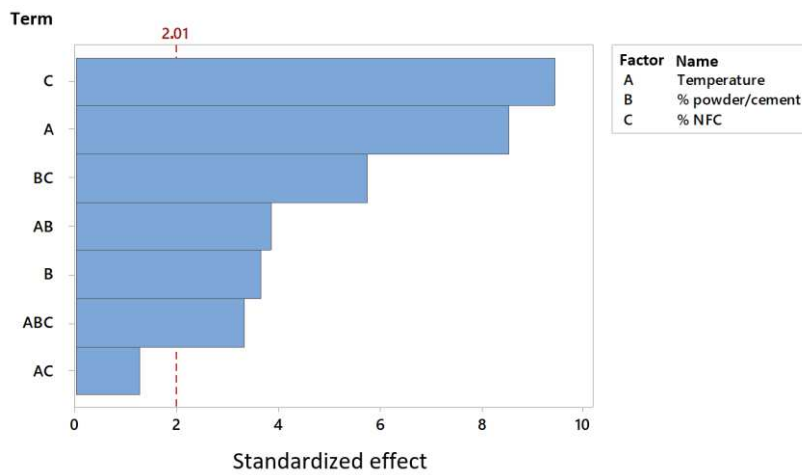
Table 9 - Tukey test for relative residual dynamic modulus factor.

Temperature*%powder/cement *% NFC	N	Mean	Grouping
200 0 0.0	4	0.919842	A
200 25 0.2	4	0.860884	B
200 25 0.0	4	0.857534	B
200 50 0.2	4	0.846465	B C
200 50 0.0	3	0.843076	B C
200 0 0.2	4	0.806565	B C
400 0 0.0	4	0.799204	C
400 25 0.0	4	0.731447	D
400 50 0.0	4	0.725940	D E
400 0 0.2	4	0.717146	D E
400 50 0.2	3	0.709600	D E
400 25 0.2	4	0.674883	E
600 0 0.0	4	0.544387	F
600 50 0.0	4	0.535817	F
600 25 0.0	3	0.535182	F
600 50 0.2	4	0.518515	F G
600 0 0.2	4	0.475736	G H
600 25 0.2	4	0.449953	H

Source: The author (2024).

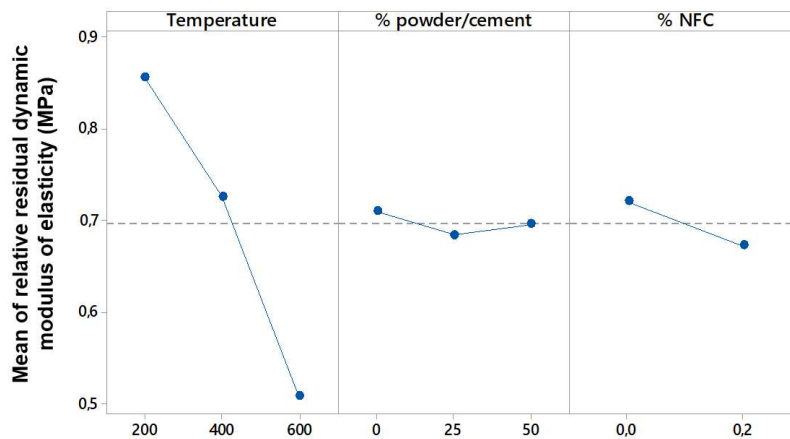
Figure 21 depicts the interaction between different factors. The interplay between powder and NFC warrants attention: as the residue amount decreases, there are greater declines in the modulus of mixtures containing NFC. Once again, this behavior can be attributed to the porosity of the matrix. The dynamic modulus serves as a parameter capable of predicting the porosity of cementitious material, with a higher modulus indicating lower porosity (E; Hatanaka, 2021). Mixtures with NFC, particularly those without or with minimal BOFS powder, and devoid of exposure to high temperatures, exhibited the highest dynamic moduli, suggesting less porous matrices. With exposure to high temperatures, these mixtures tend to experience greater thermal stresses due to their denser matrix.

Figure 19 - Pareto chart to relative residual dynamic modulus of elasticity ($\alpha=0.05$).



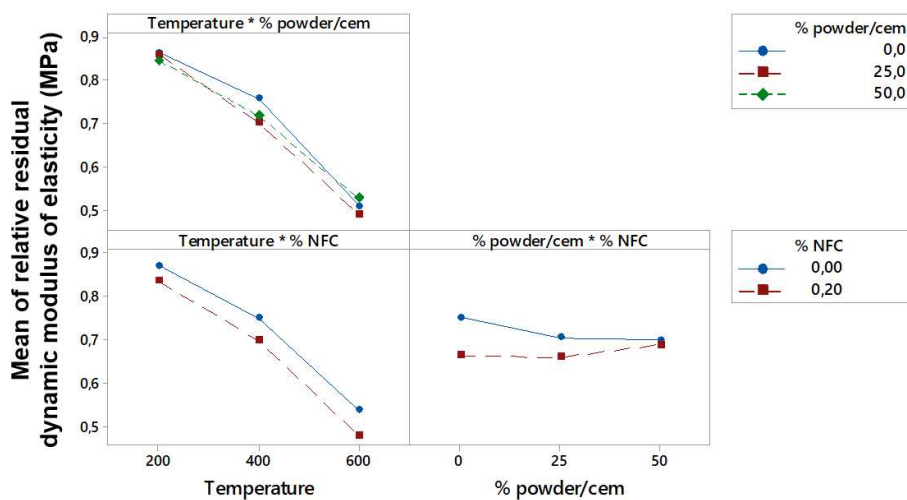
Source: The author (2024).

Figure 20 - Main Effects Plot for relative residual dynamic modulus of elasticity (temperature in °C).



Source: The author (2024).

Figure 21 - Interaction plot for relative residual dynamic modulus of elasticity (temperature in °C).



Source: The author (2024).

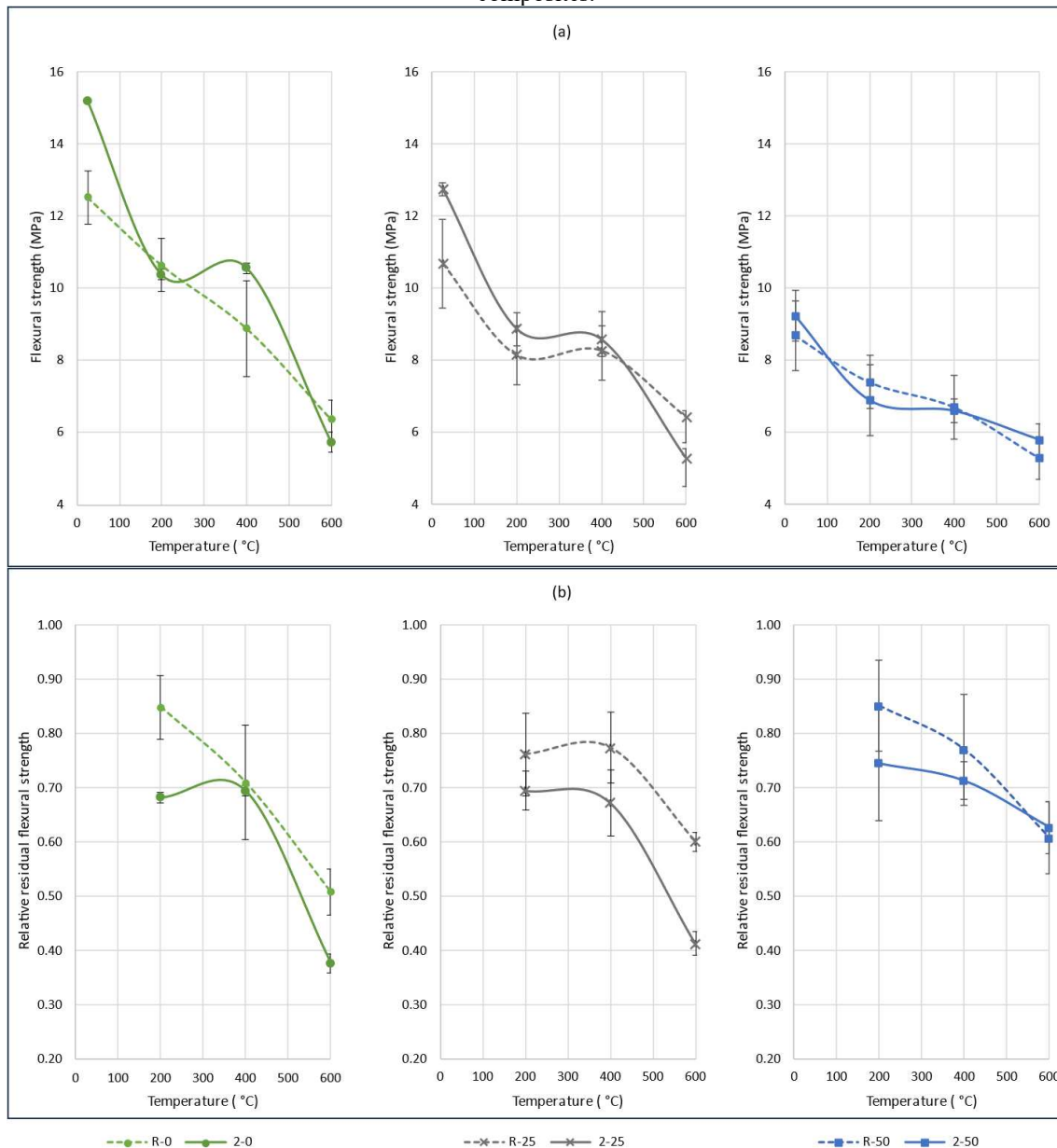
5.3.5.3. Flexural strength

Figure 22a and Table 10 illustrate the flexural strength of the mixtures under various temperature conditions. Generally, it's evident that higher powder content corresponds to lower flexural strength, with this strength decreasing as temperature rises. At 600 °C, all samples exhibit statistically similar strengths. A model with an R^2 value of 94.19% was derived through factorial analysis, wherein only the interaction between powder and NFC content was found to be not significant (Figure 23). Examining isolated factors (Figure 24), it's apparent that temperature and powder content have a negative impact on strength. Notably, the influence of temperature is less pronounced in the range of 200 °C to 400 °C. Conversely, NFC tends to positively influence flexural strength.

In Figure 25, the interaction between the three evaluated factors is depicted. It's observed that a 25% powder content combined with the addition of NFC can sustain the sample's strength within the range of 200 °C to 400 °C. However, this benefit is not observed with a 50% powder content. Hence, as seen with compressive strength, substituting powder can enhance the fire resistance of cementitious composites, provided it's not in excessive amounts. At 200 °C, the fibers remain undegraded by temperature and can act as a bridging mechanism, controlling crack propagation and stress transmission within the matrix (Afzal; Khushnood, 2021). Fiber degradation of unbleached NFC occurs between 200 °C and 400 °C (Baraka; Robles; Labidi, 2023; Jiménez-López et al., 2020), creating new voids in the matrix that alleviate internal pressures. Additionally, the addition of powder increases matrix porosity. These two factors may elucidate the plateau observed in flexural strength within this temperature range.

Figure 22b and Table 11 display the relative residual factors of the flexural strength of the mixtures at varying temperatures. These factors represent the ratio between the flexural strength of samples exposed to elevated temperatures and the strength of samples at room temperature. It's evident that as the exposure temperature increases, there's a corresponding greater loss of flexural strength. Additionally, for identical powder contents, mixtures without NFC exhibit less strength loss.

Figure 22 - (a) Flexural strength and (b) relative residual flexural strength factor of cementitious composites.



Source: The author (2024).

A model was derived through factor analysis with an R^2 value of 84.87%, wherein only the interactions between powder and NFC, and between temperature and NFC, were found to be not significant (Figure 26). Figure 27 illustrates that elevating temperature and incorporating NFC result in composites with reduced residual strength. Conversely, powder content exhibits an opposite effect, enhancing residual resistance. Figure 28 demonstrates the interaction among various factors. The sole significant interaction in the factorial model was observed between temperature and powder content, suggesting that employing BOFS powder contributes to the least loss of flexural strength.

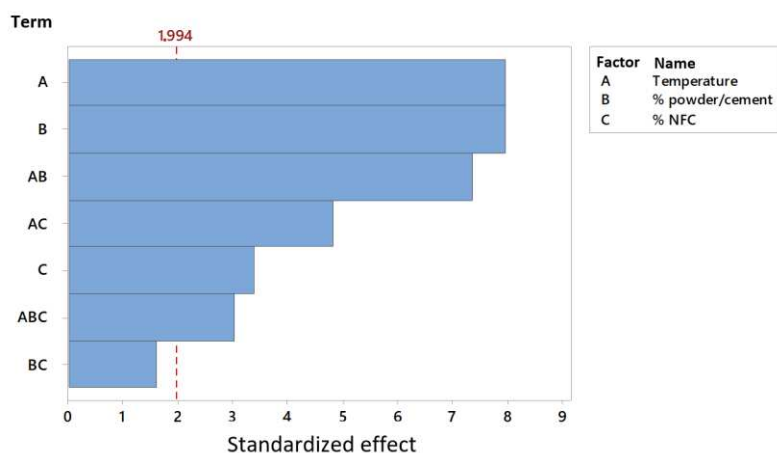
Table 10: Tukey test for the flexural strength of mixtures.

Temperature*% powder/cement * % NFC	N	Mean	Grouping
25 0 0.2	3	15.1971	A
25 25 0.2	3	12.7460	B
25 0 0.0	4	12.5204	B C
25 25 0.0	4	10.6834	C D
200 0 0.0	4	10.6372	D
400 0 0.2	4	10.5627	D
200 0 0.2	4	10.3749	D E
25 50 0.2	4	9.2381	D E F
400 0 0.0	4	8.8958	D E F
200 25 0.2	4	8.8659	D E F
25 50 0.0	4	8.6892	E F G
400 25 0.2	4	8.5769	E F G
400 25 0.0	4	8.2740	F G H
200 25 0.0	4	8.1431	F G H I
200 50 0.0	4	7.3987	F G H I J
200 50 0.2	4	6.8936	G H I J K
400 50 0.0	4	6.6977	H I J K
400 50 0.2	4	6.5951	H I J K
600 25 0.0	4	6.4244	H I J K
600 0 0.0	4	6.3678	I J K
600 50 0.2	4	5.7930	J K
600 0 0.2	4	5.7320	J K
600 50 0.0	4	5.2856	K
600 25 0.2	4	5.2715	K

Source: The author (2024).

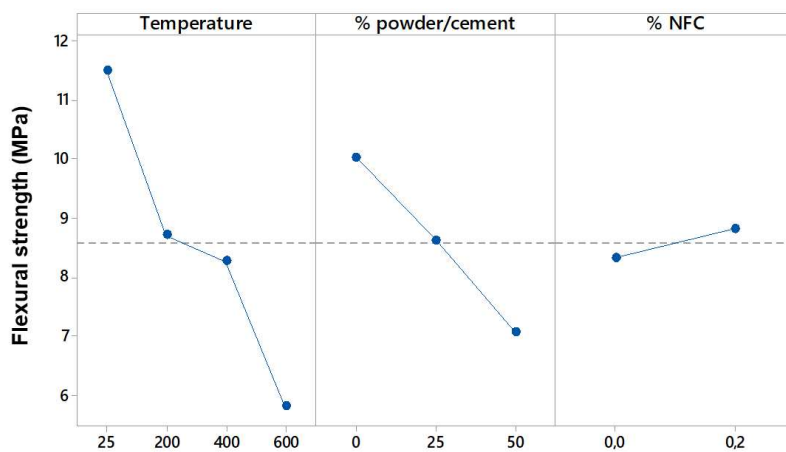
Considering the results of flexural strength, compressive strength, and dynamic modulus of elasticity, it becomes evident that producing a more sustainable cementitious material, utilizing SS aggregate as total aggregates and replacing 25% of cement with BOFS powder, proves to be an attractive solution due to its reduced loss of strength at high temperatures. Although the addition of powder diminishes mechanical strength compared to cases without powder, it remains viable for use in structural elements. At 600 °C, the compressive strength of mixtures containing 25% BOFS powder ranged from 28.0 to 32.8 MPa, while the flexural strength ranged from 5.3 to 6.4 MPa.

Figure 23 - Pareto chart to flexural strength ($\alpha=0.05$).



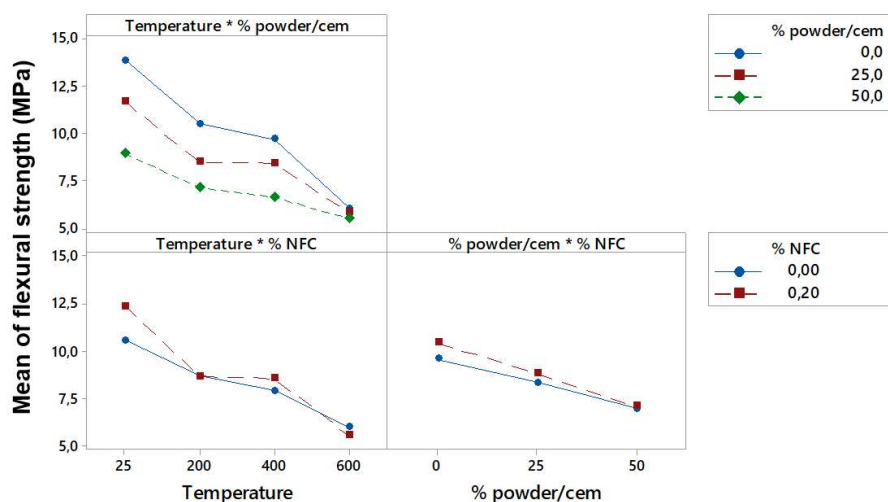
Source: The author (2024).

Figure 24 - Main Effects Plot for flexural strength (temperature in °C).



Source: The author (2024).

Figure 25 - Interaction plot for flexural strength (temperature in °C).

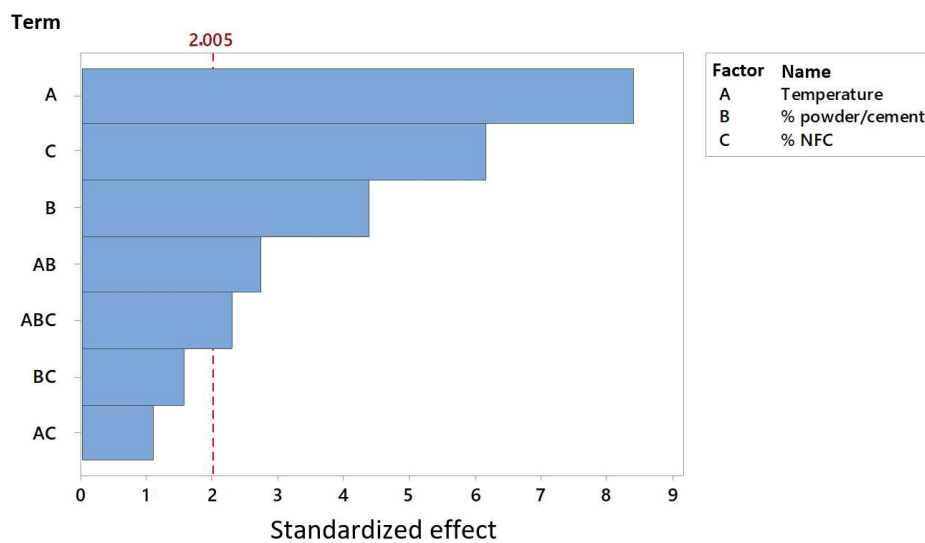


Source: The author (2024).

Table 11 - Tukey test for relative residual flexural strength factor.

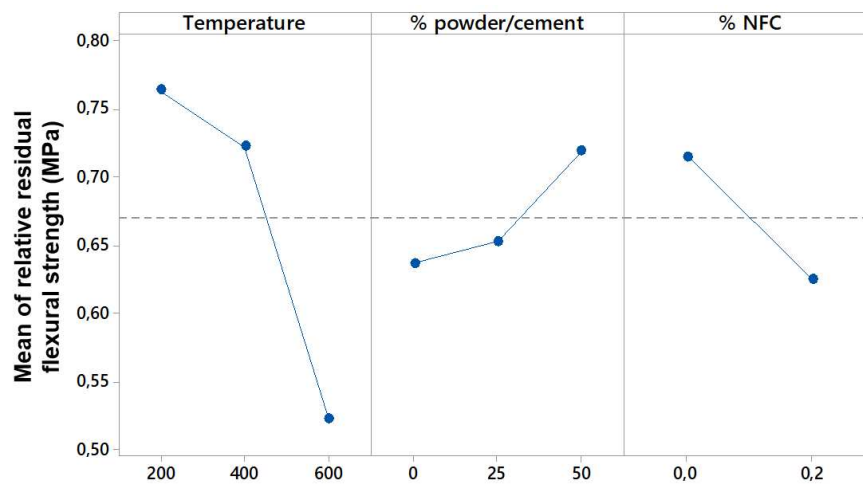
Temperature*%powder/cement *% NFC	N	Mean	Grouping
200 50 0.0	4	0.851480	A
200 0 0.0	4	0.849588	A
400 25 0.0	4	0.774468	A B
400 50 0.0	4	0.770809	A B
200 25 0.0	4	0.762217	A B C
200 50 0.2	4	0.746209	A B C
400 50 0.2	4	0.713904	A B C
400 0 0.0	4	0.710506	A B C
200 25 0.2	4	0.695582	A B C
400 0 0.2	4	0.695051	A B C
200 0 0.2	4	0.682692	B C
400 25 0.2	4	0.672913	B C
600 50 0.2	4	0.627073	B C D
600 50 0.0	4	0.608299	C D
600 25 0.0	4	0.601345	C D
600 0 0.0	4	0.508597	D E
600 25 0.2	4	0.413580	E
600 0 0.2	4	0.377179	E

Source: The author (2024).

Figure 26 - Pareto chart to relative residual flexural strength ($\alpha=0.05$).

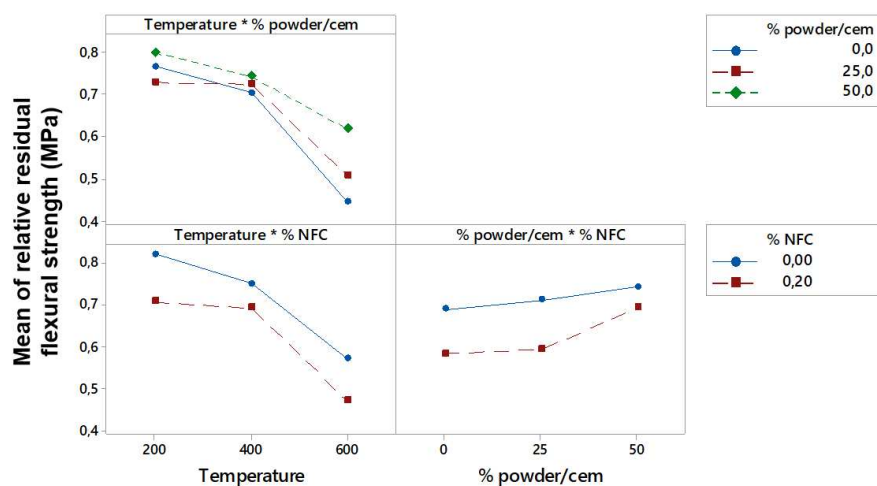
Source: The author (2024).

Figure 27 - Main Effects Plot for relative residual flexural strength (temperature in °C).



Source: The author (2024).

Figure 28 - Interaction plot for relative residual flexural strength (temperature in °C).



Source: The author (2024).

5.4. CONCLUSIONS AND FUTURE PERSPECTIVES

This study assessed the impact of incorporating BOFS powder and adding NFC on the behavior of cementitious composites at high temperatures. The key conclusions are as follows:

- vi. The utilization of a factorial design proved highly beneficial in assessing three factors simultaneously, offering a deeper comprehension of each factor individually as well as their interactions.

- vii. The incorporation of 25% BOFS powder, partially replacing cement, played a significant role in mitigating the loss of mechanical strength with rising temperatures. This can be attributed to the characteristics of this residue, which enhance the porosity of the cement matrix, thereby alleviating thermal stresses.
- viii. At lower temperatures, incorporating NFC leads to stronger specimens. However, as temperatures increase, the loss in strength becomes more pronounced, as denser matrices are more susceptible to deterioration by thermal stresses.
- ix. It was feasible to manufacture cementitious materials with a substantial incorporation of waste, both in the form of aggregate and supplementary cementitious material, exhibiting satisfactory performance at temperatures up to 600 °C.

Future work is recommended to strengthen the results obtained in this study and enhance understanding of sustainable composites at high temperatures. Suggestions include:

- iv. Investigate the behavior of composites produced under spalling conditions.
- v. Research how BOFS powder interferes with the performance and stability of NFCs.
- vi. Study the addition of new materials and waste to optimize the behavior of composites at high temperatures.
- vii. Development of methods for the large-scale production of cementitious composites.

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CHAPTER 6: GENERAL CONCLUSIONS

6.1. CONCLUDING REMARKS

The experimental research of this work enabled the production of cementitious composites with high eco-efficiency using nanofibrillated cellulose (NFC) and basic oxygen furnace slag (BOFS) aggregates and powder. The mechanical performance and eco-efficiency of these composites were evaluated according to different parameters: (i) sonication time of the NFC solutions, (ii) packing factor, (iii) age of the specimen, (iv) NFC addition content, (v) replacement of cement content with BOFS powder and (vi) temperature.

The first part of the research focused on the influence of sonication time on the dispersion and stability of NFC and the mechanical strength of cementitious composites. UV-vis, zeta potential and scanning electron microscopy techniques indicated fiber sonication favors dispersion and stability. This improvement reduced the workability of the composites in the fresh state, since NFC is hydrophilic and with better dispersion, a greater surface area of the fibers is exposed. Furthermore, there was an increase in flexural strength and eco-efficiency in the hardened state due to the bridging effect promoted by the fibers. Such results were more intense at intermediate sonication times (0.04 and 0.16 min/ml). These results guided the remainder of the research, indicating the need to control the workability of composites with superplasticizer when using NFC, as well as an ideal sonication time for producing the mixtures (0.04 min/ml).

When evaluating the packing factor, it was noted that the higher the factor, the greater the mechanical strength obtained. However, workability was a limiting factor. High packing factors correspond to lower amounts of water used, which needs to be compensated with the use of a superplasticizer to ensure adequate compaction. However, high amounts of SP drastically reduce the composites' performance. Thus, this study showed that the factor of 0.72 was the most appropriate, ensuring the best balance between mechanical strength and workability.

Regarding the age of the specimens, the study demonstrated that samples with NFC show more significant gains in flexural strength than those without NFC between 7 and 28 days. The fibers help contain the cracks propagation. Due to this same crack containment mechanism, keeping the content of cement replacement by BOFS powder constant, the mixtures with 0.2% NFC show better flexural strength than those without at

28 days. In turn, keeping the NFC content constant, greater replacement of cement with slag powder decreases mechanical strength. BOFS has less reactivity than cement, favoring the formation of a more porous matrix and thus reducing mechanical performance.

In terms of eco-efficiency relative to flexural strength, the lowest cement efficiency value (i.e., amount of cement per m³ to increase 1 MPa of strength) was obtained by the mixture with greater addition of NFC (0.2%) and greater incorporation of BOFS powder (50%). The reduction was 39.7% compared to the reference (without NFC and without powder), showing the great potential of using slag and NFC together. Furthermore, the products developed present a high volume of waste incorporation in the form of aggregates and supplementary cementitious material (between 80 and 90%), making them high-performance cementitious composites.

In the last part of the research, the performance of cementitious composites at high temperatures was evaluated. This is an important investigation into new and alternative materials. It was concluded that NFCs play a notable role in gaining mechanical strength at lower temperatures due to their role in crack control, ensuring a more cohesive and dense matrix. However, at high temperatures, this denser matrix becomes more susceptible to thermal stresses, leading to greater losses in strength. The incorporation of BOFS powder had a beneficial effect at higher temperatures. As powder mixtures are more porous, there is a relief from thermal stresses, ensuring a lower drop in strength. The incorporation of 25% powder associated with 0.2% NFC maintains compressive strength with increasing temperature, proving to be a promising alternative in the production of cementitious materials.

6.2. FUTURE RESEARCH SUGGESTIONS

Based on the results obtained in this experimental research, some future research is suggested:

- Investigate other methods for dispersing NFC, such as the use of surfactants and stabilizers, and combine them with sonication to optimize results.
- Develop techniques to maximize compaction and allow the production of composites with higher packing factors and, therefore, greater mechanical strength.

- Develop methods for producing composites on a larger scale, making the products economically viable.
- Carry out a study of cementitious composites at more advanced ages, seeking to verify whether the interaction between steel slag and NFC is beneficial or not over time.
- Investigate the effect of slag and NFC on composites subjected to spalling conditions, thus complementing the study at high temperatures.
- Expand the study to new materials and waste to increase the number of eco-efficient product options in civil construction.