PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

INFLUENCE OF CONVENTIONAL AND FUNCTIONALIZED CARBON NANOTUBES IN HYBRID ALKALINE FLY ASH PASTES THAT CONTAIN HIGH AMOUNTS OF SO_4

JEISON E. VÁSQUEZ MADARIAGA

Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the Degree of Master of Science in Engineering

Advisor:
MARCELO GONZÁLEZ H.

Santiago de Chile, October, 2020

PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

INFLUENCE OF CONVENTIONAL AND FUNCTIONALIZED CARBON NANOTUBES ON HYBRID ALKALINE FLY ASH CONCRETE

JEISON E. VÁSQUEZ MADARIAGA

Members of the Committee:
MARCELO GONZÁLEZ
NESTOR ESCALONA
ALVARO GONZÁLEZ
MAURICIO PRADENAS
Luis Rizzi Campanella
LUIS RIZZI

Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the Degree of Master of Science in Engineering

Santiago de Chile, October, 2020

To my mother Jimena and my grandparents.

AKNOWLEDGEMENTS

I want to thank, first, to my parents Jimena and Luis for their eternal support, love and patience in this long journey of study and life. I hope, with this small step, I can pay homage and pride to you. As well, I would like to thank Constanza, who is my friend and part of my family. Without her unconditional support, help and food this would not have been possible. Also, I want to thank my friends who always encouraged me to move forward and finish my thesis. And I cannot leave out of this gratitude to Juan Cristobal who was my unquestioning support in the hours of work in the laboratory, thank you for everything.

Second, I would like to thank the Fondecyt project and Professor Marcelo Gonzalez for giving me the opportunity to be part of this project to achieve my master's degree in engineering sciences.

Third, I would like to thank the Canadian Embassy, and especially Professor Martin Noël for receiving me at the University of Ottawa and allowing the generation of a collaboration between both academic institutions, which resulted in the publication of a scientific article.

Finally, thank everyone who participated in this long and sometimes complex journey.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

RESUMEN

La Industria del cemento y el hormigón es responsable del 6% al 7% de las emisiones de CO_2 a nivel mundial. Una de las alternativas que se ha explorado para reducir el nivel de emisiones de gases de efecto invernadero en la fabricación del hormigón es incorporar el uso de ceniza volante en altas cantidades como reemplazo del cemento. Para poder realizar lo anterior es necesaria la activación química de las cenizas volantes. A estas últimas pastas se les ha denominado Pastas Híbridas Alcalinas de Ceniza Volante (HAFAP). Sin embargo, debido a las nuevas regulaciones medioambientales, las cenizas volantes contienen un porcentaje mayor de sulfato (SO_4) que el permitido por las normas internacionales de hormigón y cemento, lo que conlleva a una disminución en su desempeño mecánico y de durabilidad. Por otro lado, los Nanotubos de Carbono son nanomateriales de propiedades excepcionales que se han estado investigando ampliamente. En lo particular, son cilindros compuestos de átomos de carbono con extraordinarias propiedades mecánicas, químicas, eléctricas y térmicas, pero principalmente por su naturaleza aromática son inertes y no reaccionan con el medio, lo que es relevante al momento de utilizarlos. La incorporación de Nanotubos de Carbono se ha estudiado en pastas de cemento puro y con adición de ceniza en bajas cantidades (menores al 30%), pero no se conocen sus efectos en pastas híbridas con cenizas que presenten alto contenido de sulfato. En la presente investigación, desarrollada con pastas híbridas de 70% ceniza y 30% cemento en peso, se realizaron pruebas experimentales físicas y mecánicas para evaluar y determinar el impacto de los Nanotubos de Carbono en el desempeño de este tipo de materiales. Los resultados indican que la incorporación de los nanotubos mejora la resistencia a la compresión de un 17% a un 20% y disminuye significativamente la expansión de las pastas, lo que significa una reducción volumétrica y de deterioro en las pastas híbridas alcalinas.

Palabras Claves: Nanotubos de Carbono, Ceniza Volante, Sulfato, Resistencia a la compresión, Durabilidad.

ABSTRACT

The cement and concrete industry is responsible for 6% to 7% of CO_2 emissions worldwide. One of the alternatives that have been explored to reduce the level of greenhouse gas emissions in the manufacture of concrete is to incorporate the use of fly ash in high amounts as a replacement for cement. It should be noted that in order to do the above, the chemical activation of the fly ash is necessary. These pastes have been called Alkaline Hybrid Fly Ash Pastes (HAFAP). However, due to the new environmental regulations, fly ash contains a higher percentage of sulfate (SO_4) than allowed by international standards for concrete and cement, which leads to a decrease in its mechanical performance and durability. Furthermore, Carbon Nanotubes are nanomaterials with exceptional properties that have been extensively investigated. In particular, they are cylinders composed of carbon atoms with extraordinary mechanical, chemical, electrical, and thermal properties, but mainly due to their aromatic nature they are inert and do not react with the environment, which is relevant when using them. The incorporation of Carbon Nanotubes have been studied in pure cement pastes and with the addition of fly ash in low amounts (less than 30%), but its effects in hybrid pastes with fly ashes that present high sulfate content are not known. In the present investigation, developed with hybrid pastes of 70% fly ash and 30% cement by weight, physical, and mechanical experimental tests were carried out to evaluate and determine the impact of Carbon Nanotubes on the performance of this type of materials. The results indicate that the incorporation of the Carbon Nanotubes improves the compressive strength from 17% to 20% and significantly reduces the expansion of the pastes, which means a volumetric reduction and deterioration in the alkaline hybrid pastes.

Keywords: Carbon Nanotubes, Fly Ash, Sulfate, Compressive strength, Durability.

1. STRUCTURE OF THE THESIS

Chapter Two presents an introduction to Hybrid Alkaline Fly Ash Concretes (HAFACs). The chapter gives a context, briefly describes fly ash, alkaline activation and its use in hybrid alkaline concretes. Then, a state of the art of Carbon Nanotubes is presented, as characteristics, functionalization, agglomeration and dispersion, and application in cementitious composites.

Chapter Three presents the research gap detected from the literature review and the previous background. This chapter presents the hypothesis, and general and specific objectives of this investigation.

Chapter Four presents a journal article. This Chapter evaluates the Influence of Conventional and Functionalized Carbon Nanotubes (CNTs and FCNTs respectively) in Hybrid Alkaline Pastes with Fly Ash (HAFAPs) that contain high amounts of SO_4. In this chapter it is concluded that CNTs and FCNTs manage to improve the mechanical properties of HAFAPs and significantly decrease the expansion of these pastes.

Finally, Chapter Five presents the conclusions, future works, and some contributions made throughout this research.

2. INTRODUCTION

2.1 Context

Production of ordinary Portland cement (OPC) is responsible for a significant part of global carbon dioxide (CO_2) emissions (He, Zhu, Wang, Mu, & Wang, 2019), close to 6%-7 % of the total worldwide (Shi, Jiménez, & Palomo, 2011). CO_2 is the most important greenhouse gas that causes global warming and climate change in the world (Qi, Liu, & Leung, 2019); thus, reducing emissions in the cement and concrete industry has become a priority in the area of material sciences.

There are different alternatives to be able to mitigate CO_2 emissions, options that have been proposed by the industry, especially that of the United States (Oss, Norton, & Survey, 2005) in which it is proposed, first of all, to improve the efficiency of the ovens used for the Clinker (cement raw material) generation process; however, due to the existing materials, whether it be reflective brick, thermal insulators, etc., this has not been very feasible. Secondly, this replaces the fuel used for the operation exploring renewable energy, but, these new energies do not reach the necessary temperature for the process, which is about 1,200-1,400 ° C. Third, there is the replacement of the material that contributes calcium to the cement so that it can have properties to harden; nevertheless, there are few materials that provide the necessary amount for the cement and its incorporation affects other properties.

Finally, there is the alternative of reducing the OPC content in concrete mixes by using mixed or “blended” cement (Moghaddam, Sirivivatnanon, & Vessalas, 2019), in which the OPC is replaced by one or more supplementary cementitious materials such as slag, silica fume, or coal fly ash. Fly ash (FA) is a by-product of coal-fired power plants and is widely used in the concrete industry as a supplementary cementitious material. FA has attracted great attention due to its potential to reduce CO_2 emissions and improve concrete durability. Furthermore, its ability to generate less heat during hydration is used to control adverse reactions in bulk concrete and to provide high fluidity in conventional concrete (Keun, Hwa, & Cheol, 2019), among others. Along with this, due to its high amount of alumina and silica, it is possible to make alkali activated cements, also called geopolymers, that completely replace OPC with waste products like FA (Nagaraj & Babu, 2018).

Activated alkali cements are synthesized from the chemical reaction (geopolymerization) between alkaline activators and aluminosilicates. When mixed with alkaline activators, these materials harden, producing a material with good bonding properties (Palomo, 2014). Although geopolymers have great potential for improvements in short-term durability and strength in concretes, a moderately high curing temperature (60 to 90 ° C) is required to ensure useful reaction kinetics (García Lodeiro, Donatello, Fernandez-Jimenez, & Palomo, 2016). This causes high energy consumption and makes it difficult to place on the ground. An alternative to this problem is hybrid alkaline activated fly ash cement, which aims to maximize the use of fly ash (70 to 80% by weight) and minimize the use of OPC (20 to 30% by weight) by alkaline activation (García Lodeiro et al., 2016). Due to the presence of OPC in the chemical reaction (Palomo, 2013), hybrid cement allows curing at room temperature, solving the main limitation of geopolymers. In this way, hybrid cement becomes an alternative that reduces CO_2 emissions and avoids the use of additional energy.

In 2013 new sulfur emission requirements were established worldwide and type of industry (mainly mining and thermoelectric), which caused coal power plants to change their production systems by adopting desulfurization units (Bigham et al., 2005). Although this has a positive effect on the environment, sulfate (SO_4) extracted from flue gas desulfurization (FGD) can precipitate in fly ash by modifying its chemical composition (Zunino, Bentz, & Castro, 2018). In fact, the process considerably increased the SO_4 content in the FA, over 5% by mass. In OPC, sulfates react with calcium hydroxide, which in turn produces a decrease in concrete performance due to cracking (Mohammed, Hamada, & Yamaji, 2004). This can be visualized in the following equations:

$$SO_3 + H_2O + C_3A \rightarrow (CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O\ (etringite)$$

$$SO_3 + H_2O + CH \rightarrow CaSO_4 \cdot \frac{1}{2}H_2O\ (gypsum)$$

For these reasons, the maximum SO_4 content of cement or blended cement is regulated worldwide (for example, NCh 148, ASTM C989, ASTM C150, ASTM C10, ASTM C595, IS 3812-1981, 197-2011). These standards restrict the maximum SO_4 content to 5% or less, which would also apply to these new hybrid concretes.

2.2 Fly Ash

The Fly Ash (FA), in Figure 2.1, is defined as the finely divided residue resulting from the combustion of ground or powdered coal and which is transported from the firebox through the boiler by flue gases, according to the American Concrete Institute Committee 116R. FA is a siliceous and aluminous composite, due to their pozzolanic nature, they do not present cementitious values, but in presence of humidity they react with calcium hydroxide at low temperatures, managing to form cementitious compounds. Including FA in PCC manufacture can result in material´s benefits, such as improving the workability and flow of concrete; reducing the bleeding, temperature produced by hardening concrete, shrinkage from drying and reinforcement corrosion in reinforced concrete (Malhotra & Ramezanianpour, 1994).

FA has been widely used in the cement and concrete industry (Siddique, 2010), allowing the weight of cement to be replaced by this material. In addition, concretes with 100% FA have been generated, named geopolymers but due to their difficulties in the manufacturing and curing process it has not been explored in-depth. However, a new generation of cementitious material is under development, the so-called Hybrid Alkaline Fly Ash Concretes (HAFAC) that are formed with 70%-80% of FA and 30%-20% of OPC by weight.

The extraction of FA is mainly from coal-fired thermoelectric plants, but due to the new desulfurization process, a large amount of sulfur products is retained in them, increasing their sulfate or sulfite content in their composition. However, the FA due to the type of desulfurization process (forced) its highest content is sulfate (SO_4) and in a smaller percentage the content of sulfites (SO_3^{-2}) (Córdoba, 2015). In addition, there is also sulfate in the chemical composition of Portland cement because gypsum is added to it to decrease the reaction rate to form ettringite and thus avoid the generation of false setting (P. K. Mehta & Gjørv, 1982).

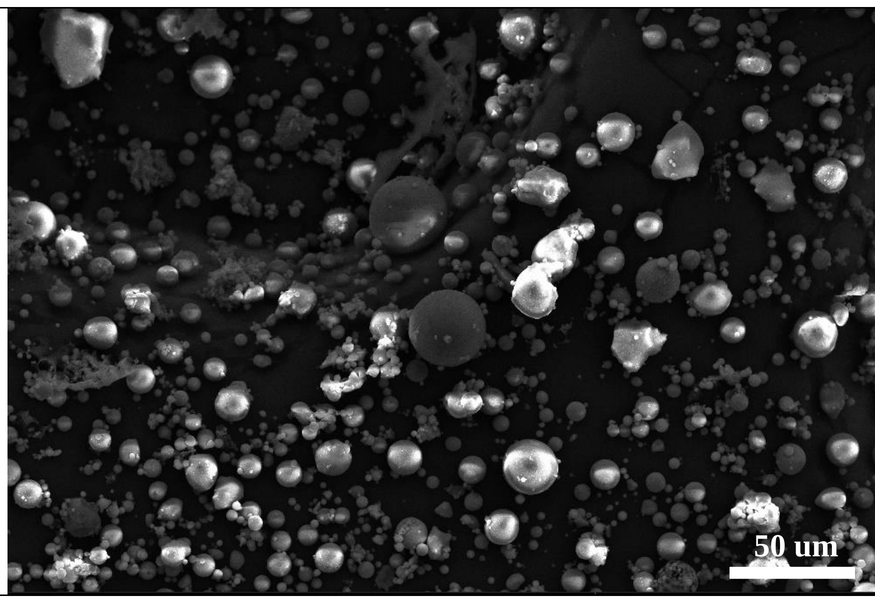

Figure 2.1 Fly Ash particles at 1300x magnification.

2.2.1 Use of Fly Ash in Hybrid Alkali-Activated Concrete

Several authors (Fu, Ye, Zhu, Fang, & Zhou, 2020; García Lodeiro et al., 2016; Khan & Sarker, 2020; Z. Li, Lu, Liang, Dong, & Ye, 2020) have shown that the use of fly ash together with an alkaline solution and soluble silicates can form a strong binder, under slightly elevated temperatures. This type of concrete is called Alkaline-Activated

Concrete, which shows excellent mechanical properties, low creep and low shrinkage (Palomo, 2014). Nagaraj & Babu (2018) have found that the amount of calcium oxide in fly ash has a significant impact on the hardened pastes of geopolymers, forming hydrated products such as calcium silicates hydrated.

It is known that the conditioning factors for obtaining alkaline aluminosilicate cements are the particle size distribution, the content of amorphous / vitreous phase and the amount of silica in the raw materials. Furthermore, higher SiO_2 / Al_2O_3 ratios are known to improve compressive strength than lower rate alkaline activating cements (Ines García-Lodeiro, Fernández-Jiménez, Blanco, & Palomo, 2008). The main characteristics that FA must have to provide good properties as a binding material in activated alkaline cements are: low CaO content, low content of unburned material (less than 5%), reactive silica content between 40%-50% and high content of vitreous phase (Fernández-Jiménez & Palomo, 2003).

2.3 Carbon Nanotubes

Carbon Nanotubes (CNTs) were discovered in 1991 by Sumio Ijima of the NEC laboratory in Tsukuba, Japan, during high-resolution transmission electron microscopy (TEM) observation of soot generated from the electrical discharge between two carbon electrodes. CNTs are cylindrical molecules with a diameter ranging from 1 nm to a few nanometers and length up to a few micrometers. Their structure consists of a graphite sheet wrapped into a cylinder (Ashby, Ferreira, & Schodek, 2009). Depending on the manufacturing process, CNTs can be single-walled (SWCNTs) or multi-walled (MWCNTs). But due to the high production costs required to manufacture SWCNTs, research is carried out with MWCNTs. Figure 2.2 shows a schematic drawing of SWCNT and MWCNT.

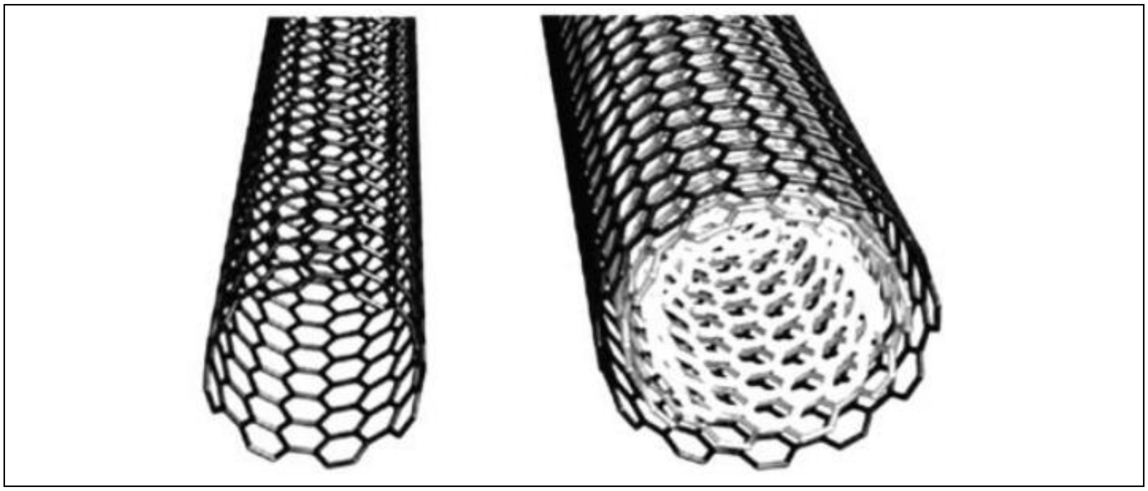

Figure 2.2 Schematic drawing of SWCNT (single-walled) and MWCNT (multi-walled) (Foldyna, Foldyna, & Zelenak, 2016)

In addition to being classified into SWCNT and MWCNT, these also depend on the form of winding of the monatomic graphite layer. The winding of the graphite layer can occur in several ways, depending on the orientation of the chiral vector which is defined as:

$$C_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$$

Where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of the hexagonal lattice of the layer and the pair (n, m) characterizes the CNT. Thus, it is also possible to know the number of hexagons that the unit cell contains, which is $N = 2(n^2 + nm + m^2)/d_r$, where d_r is the maximum common divisor between (2n + m, 2m + n). The diameter d_t and the chiral angle of the CNT (n, m) is given by:

$$d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}}{\pi} a_{C-C}(n^2 + nm + m^2)^{\frac{1}{2}}$$

$$\theta = \arctan\left(\frac{\sqrt{3}m}{2n + m}\right)$$

Where a_{C-C} is the carbon-carbon distance. From the angle theta, three types of structures or order of the graphene layer can be identified. If m = 0 the CNTs are called "zigzag", if n = m they are called "armchair" and otherwise they are called "chiral". Figure 2.3 shows a schematic diagram of the basic structures of CNTs

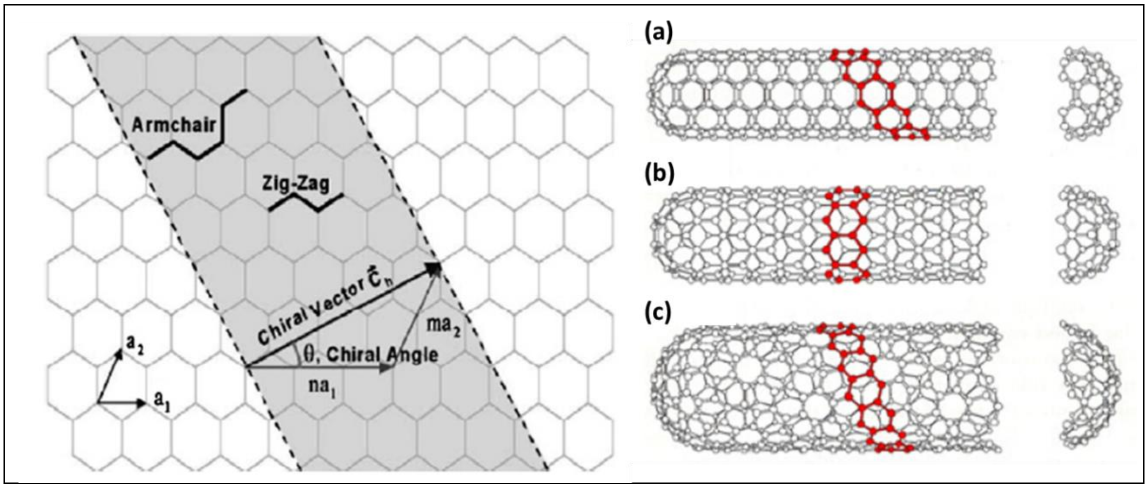

Figure 2.3 Schematic diagrams of the basic structures of CNTs. (a) armchair, (b) zigzag, (c) chiral. Adapted from Ma, Siddiqui, Marom, & Kim (2010).

Various authors (Chaipanich, Nochaiya, Wongkeo, & Torkittikul, 2010; Makar, Margenson, & Luh, 2005; Tafesse & Kim, 2019) highlight the excellent properties that CNTs have, whether mechanically, physically, electrically, chemically, among others. In mechanical terms, CNTs have exceptionally high properties, because the C-C bond is one of the strongest bonds in nature. With this, the CNTs reported that the average Young's modulus of MWNT was 1.0-1.2 TPa (Chaipanich et al., 2018). Furthermore, CNTs have a tensile strength of 50-200 GPa and yield strength of 10-60 GPa. The physical properties are attributable to their small size, since they are nanometric materials and therefore function as a filler between the other materials and the spaces that are generated. On the other hand, electrical properties of CNTs are attributed to its one-dimensional characteristic and peculiar electronic structure of graphite. In particular, this is closely related to the quantum confinement of electrons, which are distributed normal to the tube axis (Ashby et al., 2009). The electrons are restricted in the radial direction by the graphene sheet and therefore only propagate along the axis of the tube. This means that the electrons inside the tube travel freely, for this reason the resistivity of the CNTs is extremely low (Ashby et al., 2009). Finally, the main chemical property of CNTs is that they are chemically stable, this is due to their aromatic nature because of the type of C-C bond (Ma et al., 2010). This property allows CNTs to interact with the environment without generating changes or chemical reactions that are not desirable.

2.3.1 Functionalization

Due to carbon atoms are chemically stable in their C-C bond, and to the aromatic nature, CNTs are inert and the form of interaction they present with the medium is simply through Van der Waals forces. These forces are weak and unable to generate efficient stress transfer to improve the performance of nanocomposites. Therefore, the alternative that has been developed is to modify the surface of the CNTs to improve its adhesion and interaction properties with the environment, which is known as functionalization.

Chemical functionalization (Ma et al., 2010) is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. It can be performed at the termini of the tubes or at their sidewalls. Direct covalent sidewall functionalization is associated with a change of hybridization from sp2 to sp3 and a simultaneous loss of p-conjugation system on graphene layer. In the Figure 2.4 can be observed types of functionalization of CNTs. Acid treatment is the most widely used technique for the functionalization of CNTs. This treatment is carried out with H_2SO_4 and HNO_3 at temperatures above 325° C and form carboxylic acid groups on the surface CNT with higher dispersion characteristics in cementitious composites.

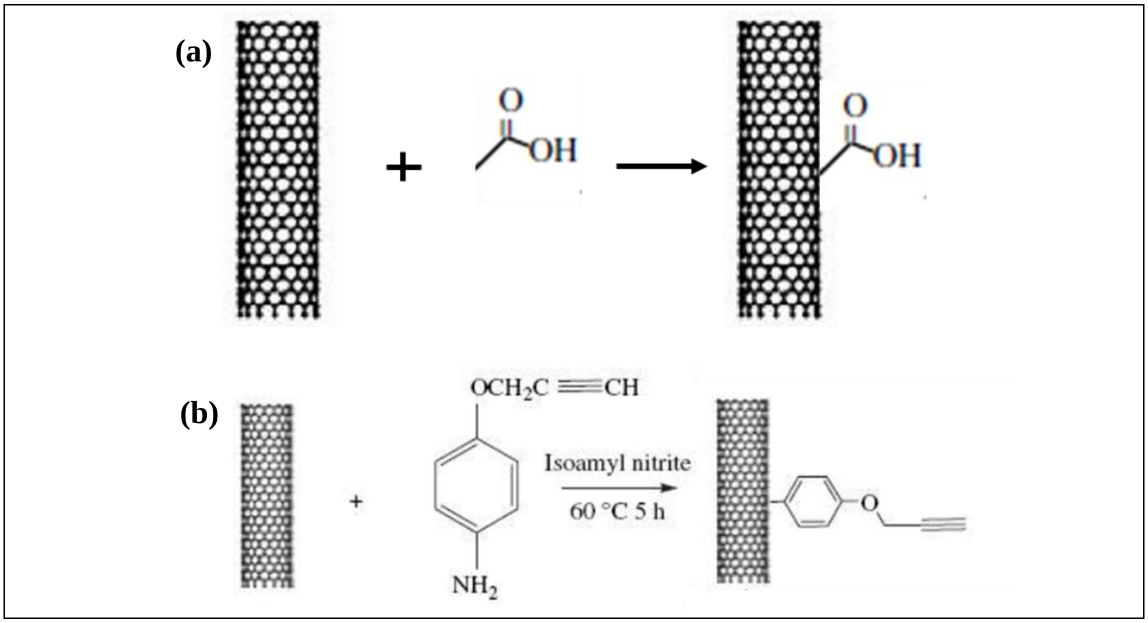

Figure 2.4 Types of functionalization of CNTs. (a) with -COOH group, (b) polyurethane group. Adapted from Salavagione (2011).

2.3.2 Agglomeration effect and dispersion

CNTs may present a lower performance in all their properties (compared to theory) on account of the effect of agglomeration. This effect occurs in CNTs due to their high aspect ratio and flexibility, tubular shape and, significantly, the Van der Waals interaction. Van der Waals forces increase in CNTs due to the high specific surface area of CNTs, which causes agglomerated CNTs particles. The effect of agglomeration generates discontinuities in compounds with incorporation of CNTs and therefore weaken or worsen performance.

To reduce the negative effects of agglomeration, there are dispersion methods for CNTs. Ultrasonication is the most widely used method. Ultrasonication converts line voltage into mechanical vibrations. The converted mechanical vibrations are then transferred to the fluid from the probe creating pressure waves, which increases fluid temperature by cavitation (Hielscher, 2005). The ultrasonication of CNT induces high local shear, particularly on the tube end, creating spaces among the particles, and therefore has been an effective means of dispersing CNT particles in liquid media with a low viscosity, i.e., water, acetone and ethanol (Kim et al., 2019). However, the use of ultrasound for a long time can damage the CNTs, so authors (Konsta-Gdoutos & Aza, 2014) recommend a study of the dispersing capacity of each CNT to improve their performance and reduce agglomeration. Figure 2.5 shows an ultrasonicator of ultrasonic probe used for this research.

Figure 2.5 Ultrasonicator of ultrasonic probe used for this research.

2.3.3 Application in cements composites

The incorporation of CNTs in cementitious composites has been widely studied. Either as a reinforcement of the cementitious matrix, autogenous shrinkage reducer, piezoresistive sensor, electromagnetic waves shielding material, heating material, among other uses.

The CNTs in cementitious composites have obtained good results according to various studies (Makar et al., 2005; Safiuddin, Gonzalez, Cao, & Tighe, 2014; Shah, Hou, & Konsta-Gdoutos, 2015), achieving improvements in compressive strength of 20% and flexural strength of 25% with respect to the control (G. Y. Li, Ming, & Zhao, 2005). Besides, in investigations with 20% FA and 80% cement, it has been observed that the addition of CNTs in the matrix has increased the compressive strength between 8% and 10% (Chaipanich et al., 2010). All this occurs because the CNTs behave as reinforcement in the micro-cracks that are generated in the cement compounds, managing to generate crack bridges and identifying fibers in the matrix (Makar et al., 2005). Figure 2.6 shows the behavior of CNTs in micro-cracks.

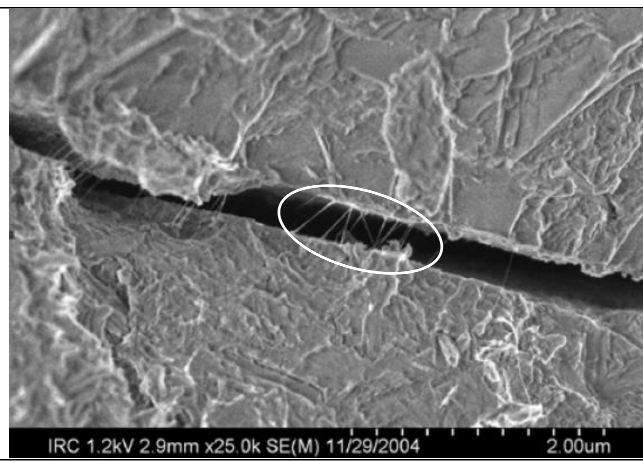

Figure 2.6 Behavior of CNTs in micro-cracks (CNTs in circle) (Makar et al., 2005).

3. SUMMARY OF CONDUCTED WORK

3.1 Research gap

According to several authors (Gartner, 2004; P. K. Mehta & Gjørv, 1982; Siddique, 2010), the use of FA in concrete and as a partial replacement for cement is an alternative that should be considered for reducing greenhouse gases, especially CO_2. The use of fly ash must be in high quantities in order to generate a significative change in the CO_2 emissions produced by the cement industry. However, if part of the cement matrix is formed by fly ash, it is not capable of reaching the mechanical performance of a pure cement paste. In addition, in the last decade the content of sulfate (SO_4) in the fly ash present in the interior FA has increased due to new environmental desulfurization regulations. To mitigate or reduce these adverse effects of FA and its high sulfate content, the alternative of incorporating CNTs is promising. However, the effect of the incorporation of conventional and functionalized CNTs has not been studied in hybrid pastes.

3.2 Hypothesis

The incorporation of low amounts of conventional and functionalized CNTs increase compressive strength and decrease expansion of hybrid FA/Cement pastes.

3.3 Objectives

The main objective of this thesis is to understand the effects of incorporating CNTs in the mechanical, physical and chemical properties of HAFAPs. The specific objectives are:

1) To evaluate the impact on compressive strength due to the incorporation of CNTs in alkaline hybrid pastes with a high content of SO_4.
2) Determine the impact on the durability of alkaline hybrid pastes due to the incorporation of CNTs.
3) To understand physical-mechanical behavior through chemical analysis of HAFAPs.

3.4 Methodology

To understand the effects of incorporating CNTs in the mechanical and chemical properties of Hybrid Alkaline Fly Ash Pastes (HAFAPs) twenty-seven pastes were made. All the pastes mixes were cast at binder with 70% FA and 30% OPC weight. Three control HAFAPs mixes without CNTs for FA-Colbun, FA-Ventana 3 and FA-Ventana 4, other 24 pastes were added 0.005%, 0.01%, 0.03% and 0.05% for conventional and functionalized CNTs to each type of FA (Colbun, Ventana 3 and Ventana 4). The main test to assess sulfate resistance was adapted from Ferraris et al. (2012) who proposed a faster test to assess sulfate resistance of hydraulic cement (called mini-bar test). Also, several experiments were carried out to assess the mechanical, physical and chemical behavior of pastes such as compressive strength, Scanning Electron Microscopy (SEM), Fourier-Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). To determinate the optimal dispersion time, the UV-vis experiment was carried out. In figure 3.1 can observe a summary of the methodology used.

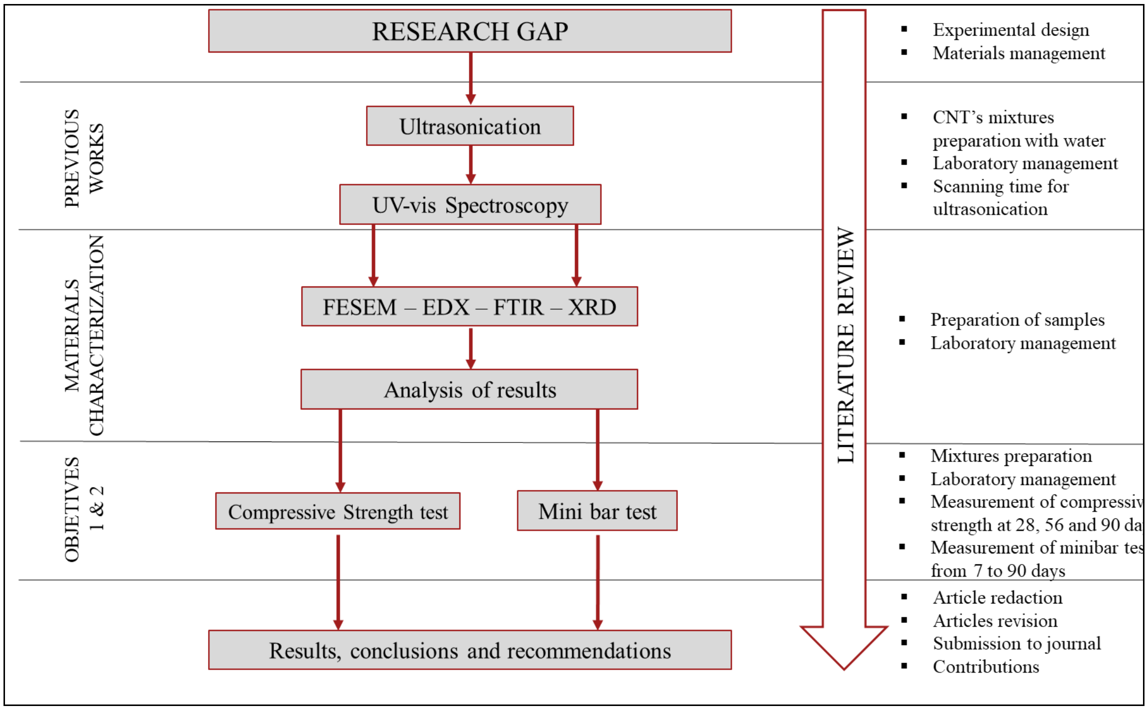

Figure 3.1 Thesis methodology summary.

4. INFLUENCE OF CONVENTIONAL AND FUNCTIONALIZED CARBON NANOTUBES IN HYBRID ALKALINE PASTES WITH FLY ASH THAT CONTAIN HIGH AMOUNTS OF SO_4

4.1 Abstract

This research investigates the effect of incorporating conventional and functionalized carbon nanotubes into a cementitious matrix made of 30% cement and 70% fly ash with high amounts of sulfate. Carbon nanotubes were added in different proportions, and the mechanical and physical properties were evaluated through a compressive strength and minibar test, respectively. Chemical and physical characterizations of pastes were also conducted. The results showed that carbon nanotubes improve both the mechanical resistance of pastes and their performance in terms of expansion. This advanced characterization allowed a better understanding of the material's performance.

Keywords: Carbon Nanotubes, Functionalized, Fly Ash, Compressive strength, Expansion.

4.2 Introduction

The production of ordinary Portland cement (OPC) is responsible for a significant part of global carbon dioxide (CO_2) emissions (ASOCEM, 2018; He et al., 2019), close to 5–7% of total emissions (Gartner, 2004; Worrell, Price, Martin, Hendriks, & Meida, 2001). CO_2 is the most important greenhouse gas associated with global warming and climate change (Qi et al., 2019); therefore, reducing CO_2 emissions during the production of cement and concrete has become a priority in the industry (Scrivener, John, & Gartner, 2018).

There are different alternatives to reducing the CO_2 footprint of concrete materials (Oss et al., 2005). One of the most efficient approaches is to partially replace OPC with supplementary cementitious materials (SCM), in particular with fly ash (FA). This type of SCM has been widely investigated due to its potential to improve the mechanical properties and reduce the CO_2 footprint of concrete (García Lodeiro et al., 2016; P. Kumar Mehta, 2004; Rashad, 2015; Siddique, 2004). Fly ash is a by-product of coal-fired power plants, and when locally available it is used in Portland cement concrete (PCC) as a SCM (Chaipanich et al., 2010). Fly ash meets the requirements of ASTM C618 (ASTM, 2020).

In addition to the environmental benefits of fly ash (Ferone et al., 2013; Mena, González, Remesar, & Lopez, 2020; Siddique, 2010), including fly ash in PCC mixtures improves the workability and flow of fresh concrete, reduces the bleeding, controls the setting temperature, prevents shrinkage from drying, and mitigates corrosion in reinforced concrete (Malhotra & Ramezanianpour, 1994; P. K. Mehta & Gjørv, 1982). In general, fly ash can improve the durability of concrete (Bouzoubaâ, Zhang, & Malhotra, 2001).

Although fly ash improves many technical properties of conventional PCC, a high content of fly ash decrease early age strength (strength in the first days); therefore, fly ash content in PCC is restricted for many practical applications (Sharma, Susan, Kothiyal, & Kaur, 2018). Large amounts of fly ash influence the hydration kinetics, thus affecting the setting time of the material and impacting the construction process.

Hybrid alkaline fly ash pastes (HAFAPs) are a new generation of binders that minimize the use of ordinary Portland cement (OPC), or clinker, and maximize the use of fly ash without negatively affecting the early properties of materials. This approach allows the production of hybrid alkaline fly ash concrete (HAFAC) that combines high amounts of fly ash (70 to 80 wt%) and low amounts of OPC (20 to 30 wt%). The incorporation of Portland cement is essential because it allows curing at environmental temperatures to obtain adequate setting time (García Lodeiro et al., 2016). HAFAC becomes a potentially sustainable alternative that reduces CO_2 emissions and avoids the use of additional energy.

Currently, new desulfurization environmental requirements in different power plants require the adoption of new processes (Bigham et al., 2005) that influence the properties of fly ash. In these processes, the SO_2 gas reacts with $CaCO_3$ to produce $CaSO_3$ $2H_2O$, which can be converted to $CaSO_4$ $2H_2O$ or $CaSO_3$ ½ H_2O. Since the main desulfurization process is forced, 90% of the products of these reactions are $CaSO_4$ $2H_2O$ (Córdoba, 2015). This entire process removes sulfate from the environment, but this sulfate then precipitates in fly ash. In the fly ash, there are both types of sulfur; sulfate (SO_4) and sulfite (SO_3), but the most harmful is sulfate (SO_4) due to its origin from the desulfurization process. Fly ash with a high amount of sulfur can cause chemical issues such as sulfate attack or efflorescence (Mastali et al., 2019; Ríos, González, Montes, Vásquez, & Arellano, 2020; Zhang, Provis, Ma, Reid, & Wang, 2018), thus compromising the integrity and durability of HAFACs.

Several reasons can explain the interest in investigating the behavior of high-sulfur fly ash, including the necessity of learning more about the behavior of this material that is currently discarded in landfills, and the possibility of establishing new strategies for using nanotechnology to reuse high-sulfate fly ash and moving the construction industry to a circular economy.

Nanotechnology offers new possibilities to improve the behavior of materials. Several authors (Chaipanich et al., 2010; Makar et al., 2005; Tafesse & Kim, 2019) have reported that carbon nanotubes (CNTs) are promising because they have a tensile strength of 50–200 GPa, Young's modulus of 1–1.2 TPa, and yield strength of 10–60 GPa. Due to their mechanical properties, carbon nanotubes have been used as a reinforcing material for various matrix composites (Chaipanich et al., 2010). Furthermore, the carbon atoms of nanotubes are chemically stable and inert due to the aromatic nature of the bond (Ma et al., 2010). The two main types of carbon nanotubes are (a) single-walled carbon nanotubes, which are cylinders consisting of a single layer of graphene; and (b) multi-walled carbon nanotubes, which consist of multiple rolled layers of graphene (Ma et al., 2010). Carbon nanotubes can also be modified to improve their chemical properties by adding functional groups to their surface (Mendoza, Sierra, & Tobón, 2013); these types of CNTs are called functionalized carbon nanotubes (FCNTs). Finally, some authors (Ma et al., 2010; Manzur, Yazdani, & Emon, 2016) have recognized that nanomaterials provide other benefits, such as the nucleation effect, which promotes better hydration products in conventional PCC, and possible improvements to the setting time of conventional concrete because of changes in hydration kinetics.

So far, the potential impact of CNTs on the strength, mechanical properties, and durability has not been investigated when fly ash with a high SO_4 content (> 5%) is used in HAFAPs. Therefore, this research focuses on evaluating those properties by incorporating two types of carbon nanotubes, conventional and functionalized, into HAFAPs that use fly ash with a high amount of sulfate (SO_4 > 5%).

4.3 Material and Methods

4.3.1 Materials

The cement used for this study was ordinary Portland cement (OPC) type I according to ASTM C150 (Apparatus & Inor-, 2020). The fly ashes investigated were collected from three different Chilean power plants: Colbun (FA-CB), which contains a low amount of SO_4 (< 5%), and Ventana unit 3 (FA-V3) and Ventana unit 4 (FA-V4), both of which contain high amounts of SO_4 (> 5%) according to ASTM C618-19 (ASTM, 2020). Sodium hydroxide (NaOH) in flakes with 99% purity was used to produce the sodium hydroxide solution. Laboratory-grade sodium silicate solution (8.0% Na_2O and 26% SiO_2 by mass) was also used as an activator with a 2.5 silica modulus (SiO_2/Na_2O ratio). Also used were multi-walled carbon nanotubes (for simplicity, they will be called CNTs), both conventional and with COOH functional groups (FCNTs). According to the manufacturer, the CNTs and FCNTs have an outside diameter from 30 nm to 50 nm, an inside diameter from 5 nm to 10 nm, and a length from 10 um to 20 um. A superplasticizer (SP) and a sonication process were used to disperse both types of CNTs.

4.3.2 Characterization Techniques

4.3.2.1 UV-visible spectroscopy (dispersion)

UV-visible spectroscopy was used to determine the optimum sonication time for fully dispersing the CNTs in the mixing water. In this method, different samples of CNTs in water with superplasticizer were prepared similarly and were sonicated for varying times, from 10 minutes to 50 minutes. Each sample was then placed in the UV-vis absorption spectrophotometer (Shimadzu, Model UV-1280) and passed through a beam of light; the resulting wavelength was measured. This procedure is an indirect method for measuring dispersion (Yu, Grossiord, Koning, & Loos, 2007).

4.3.2.2 X-ray diffraction (XRD)

XRD was performed to determine the mineral composition of the OPC and fly ash, and it was also performed on hardened pastes after 90 days. The samples were generated by dry milling, achieving a powder with a particle size distribution smaller than 10 um. A Bruker D2 Phaser diffractometer was used, working at 30 kV/10 mA in the range of 10° 90° and using a step size of 0.01 for every 1.25 s. The XPowder software was used to quantify the phases present in the samples. Structural data from the PDF-4+ database were used to construct a calculated profile that is as similar as possible to the measured profile of the sample. By refining the model, the differences between the two profiles were minimized and each phase was quantified. The percentage of amorphous material present was determined by modelling a standard in this way and then inputting into the software the actual percentage of standard that was added.

4.3.2.3 Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (FESEM-EDX)

A FESEM analysis was used to study the morphology of the raw materials and the physical-mechanical behavior of the CNTs. The analysis of FESEM and EDX was applied to the samples of hardened pastes after carrying out the compressive strength test at 90 days. For this, samples were taken from the center of the broken specimen, coated with a 4 nm layer of gold, and placed on a platform. For the EDX analysis, the tested area corresponded to the full mapping area covered by the image. A Zeiss EVO MA10 microscope was used to obtain high-resolution images.

4.3.2.4 Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was performed to understand the hydration process of the mixtures and of the products obtained. The samples were obtained after a compressive strength test at 90 days. The samples, in powder form, were pressed with KBr to form pellets. FTIR spectra were recorded from 4000 cm^{-1} to 450 cm^{-1} using a spectrometer (Shimadzu IRTracer-100).

4.3.2.5 Mini bar test

A rapid sulfate test was applied to evaluate the sulfate resistance (or durability) of the HAFAPs; it was adapted from Ferraris et al. (Ferraris, Stutzman, Peltz, & Winpigler, 2005). The dimensions of the bars were 10 mm × 10 mm × 40 mm, and the ends of the bars have embedded pins. After 24 h, the bars were removed from the mold and left to cure in lime water in a curing chamber at 23 °C ± 2 °C for 3 days. Then, the bars were removed from the lime water and epoxy was placed on their ends. The samples were returned to the lime water for 11 days. The bars were then removed from the lime water, and the initial measurement was taken with a comparator reading according to the procedure and left in a sulfate solution, 50 g/L Na_2SO_4. The first measurements were made five times a week for the first two weeks and then once a week for three months. **Figure 4.1** shows some of the equipment used in the material characterization.

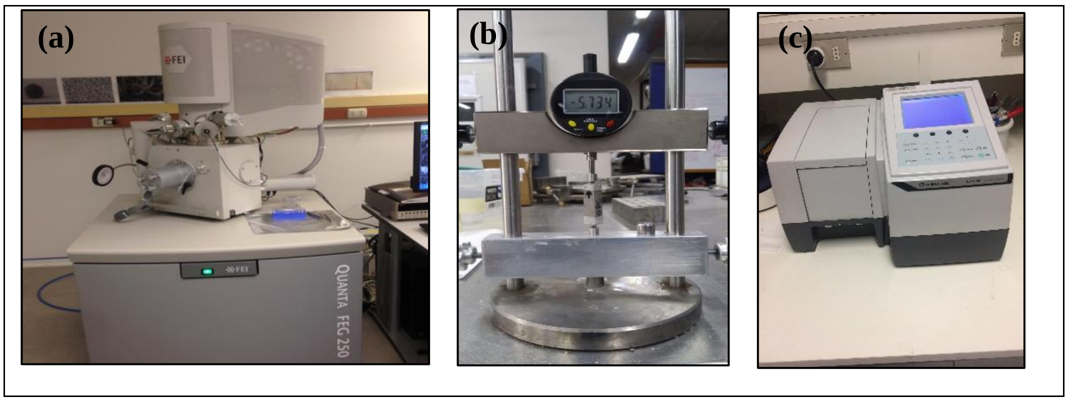

Figure 4.1 (a) FESEM, (b) mini bar test and (c) UV–vis absorption spectrophotometer.

4.3.2.6 Compressive Strength

Compressive strength was tested according to ASTM C109 in 50 mm × 50 mm × 50 mm cubes. After 24 h the samples were removed from the mold and left in a curing chamber with relative humidity of 95 ± 1%. Three samples for each age were tested for compressive strength at 7, 28, 56, and 90 days, with a constant load rate of 1.8 kN/s for all cases.

4.3.3 Experimental Design, Mixing, and Casting

4.3.3.1 Experimental Design

The composition of the paste formulations is presented in **Table 4.1**. In general, a total of 27 combinations were prepared and tested. All paste mixes were cast at binder with 70% fly ash and 30% OPC by weight. The three HAFAP controls were FA-CB, with low sulfate, and FA-V3 and FA-V4, with no CNTs. The other 24 pastes were added at 0.005%, 0.01%, 0.03%, and 0.05%, according to **Table 4.1**, where YY represents the type of FA (CB, V3, V4) and X represents whether the CNT was conventional or functionalized (C or F, respectively). The chemical ratio was 2.5 to optimize the geopolymerization, and the mass ratio of binder to chemical activator was 1:2.5.

Table 4.1 Composition of pastes.

Mix ID	**W/B**	**FA/C**	**% CNT**	**Na_2SiO_3/ NaOH**
FA-YY-0X	0.48	70/30	0	2.5
FA-YY-005X	0.48	70/30	0.005	2.5
FA-YY-01X	0.48	70/30	0.01	2.5
FA-YY-03X	0.48	70/30	0.03	2.5
FA-YY-05X	0.48	70/30	0.05	2.5

4.3.3.2 Mixing and Casting of Pastes

The CNTs were initially dispersed using sonication with part of the mixing water and the superplasticizer for 10 min, and then the fly ash and OPC were dry mixed for 2 min. Finally, the alkaline activator was added to the CNT solution and mixed for another 3 min. The mixtures were poured into steel cubic molds of 50 mm according to ASTM C109 and into the molds for the sulfate resistance test.

4.4 Results and Discussion

4.4.1 Materials characterization

The images of the materials were obtained by field emission scanning electron microscopy (FESEM), as shown in **Figure 4.1**. On the other hand, **Tables 4.2** and **4.3** show the chemical and mineralogical composition obtained with X-ray diffraction (XRD). **Figure 4.2** shows the spherical shape of the fly ash and the cylindrical shape of the CNTs.

It is important to note that the amorphous content present in the fly ash studied is relatively low compared to that suggested by some authors (Keun et al., 2019; Rashad, 2015). The morphology of fly ash affects its reactivity and will therefore affect compressive strength and durability (García Lodeiro et al., 2016). On the other hand, conventional and functionalized CNTs provide a specific surface for the development of reaction products.

Table 4.2 Chemical composition of OPC and FA.

	OPC	FA - CB	FA - V3	FA - V4
$SiO_2 + Al_2O_3 + Fe_2O_3$	29.3	66.8	69.0	68.7
SiO_2	21.4	44.5	43.2	41.9
MnO	0.05	0.1	0.04	0.04
Fe_2O_3	3.3	10.0	3.1	3.5
K_2O	0.5	3.5	1.2	1.3
SO_3	1.9	0.02	12.8	13.9
CaO	65.2	1.4	15.2	14.7
TiO_2	0.3	1.1	0.6	0.6
Al_2O_3	4.5	12.2	22.7	23.3
SrO	0.1	-	0.04	0.05
LOI	1.6	6.5	5.8	6.3

Table 4.3 Mineralogical composition of FAs.

	Crystalline (%)				Amorphous (%)
Material	Quartz	Mullite	Portlandite	Sum	Sum
FA-CB	17.8	11.6	0	29.3	70.7
FA-V3	13.2	2.3	21.7	37.2	62.8
FA-V4	15.8	2.1	20.3	38.2	61.3

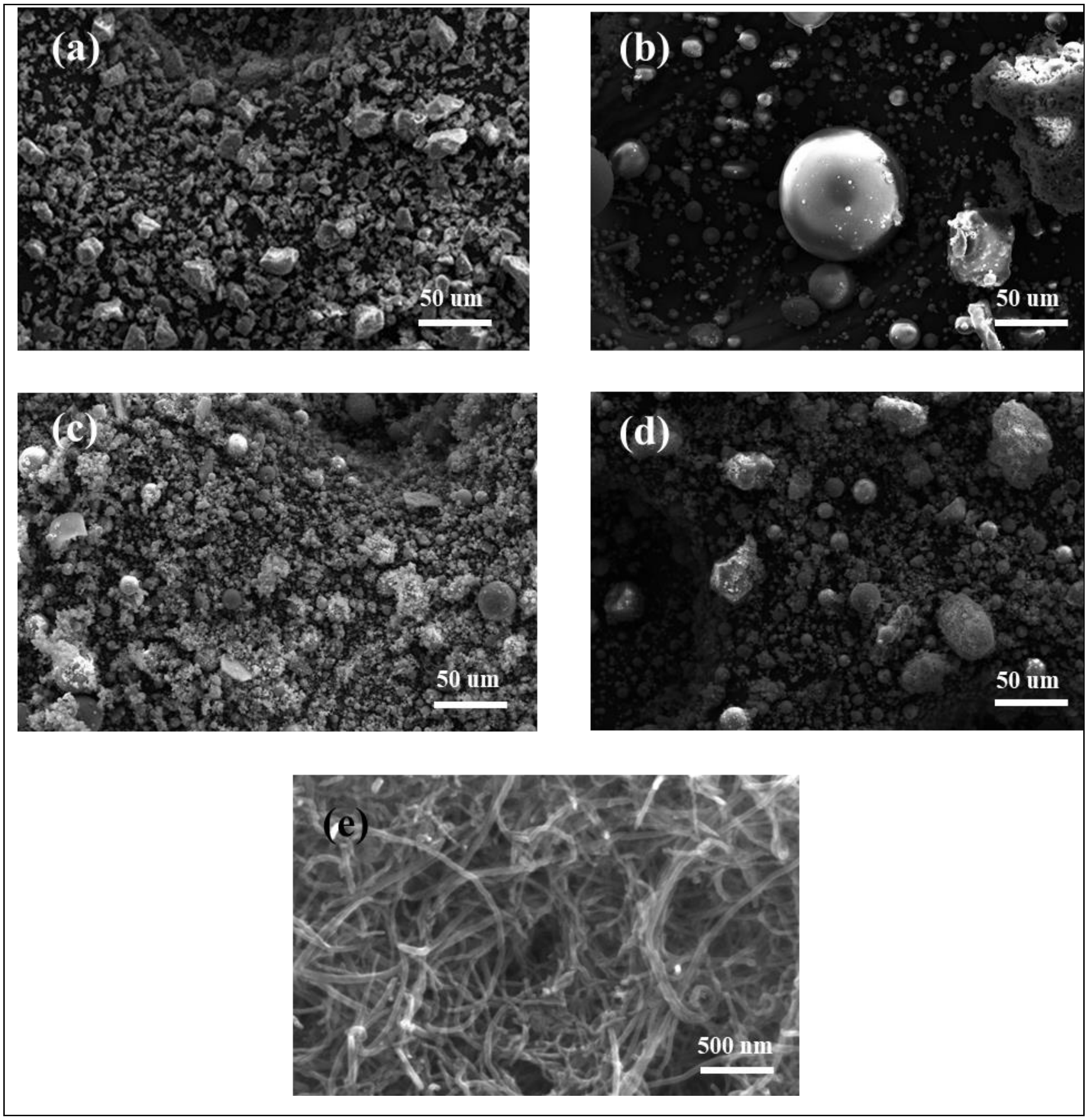

Figure 4.2 FESEM images of (a) OPC, (b) FA-CB, (c) FA-V3, (d) FA-V4 and (e) CNTs.

4.4.2 Dispersion

Figure 4.3 shows the UV-visible spectra of the aqueous solution incorporating CNTs and a superplasticizer. Five curves represent the CNTs sonicated at different times. Superplasticizer was included to improve the dispersion of these (Kim, Nam, Yoon, & Lee, 2018). The agglomerated CNTs are active in a wavelength between 200 nm and 800 nm, due to the spaces generated between them by the sonication (Yu et al., 2007). With this, it is possible to relate the level of dispersion of the CNT and the absorption spectrum in a direct way; that is, the higher the level of absorption, the greater the degree of dispersion of the CNTs (Alafogianni et al., 2016). After sonication, there are peaks between 200 nm and 300 nm, decreasing as the sonication time of the sample increases (Figure 3). With this procedure, it was determined that the optimal time to sonicate the CNT was 10 min; this time allows high absorbance to be obtained and is optimal for saving energy in the process and reducing associated costs.

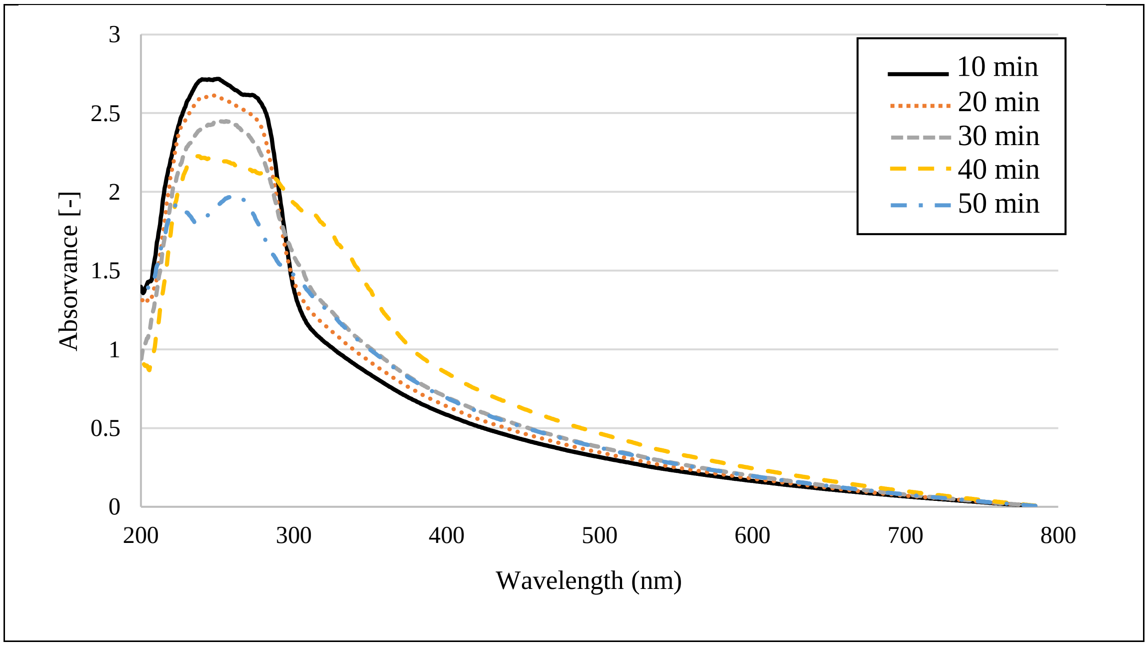

Figure 4.3 UV–Vis spectra of CNT-incorporated to aqueous solutions to different times.

4.4.3 Mini bar test

Figure 4.4 shows the expansion results of the minibar test for the control pastes measured until 90 days; the expansion results incorporate error bars with a ± standard deviation. It is important to highlight that expansion results represent the ability of cementitious materials to resist sulfate attack, which is an indication of the paste's durability. According to the results, the three pastes have an expansion greater than or equal to 0.4%; the FA-CB control paste presents the higher expansion. This behavior can be explained by the calcium content in the fly ash. FA-CB has a low calcium content compared to FA-V3 and FA-V4, which directly affects the expansion of the specimens. Note that all control samples maintained their integrity until the end of the test (90 days).

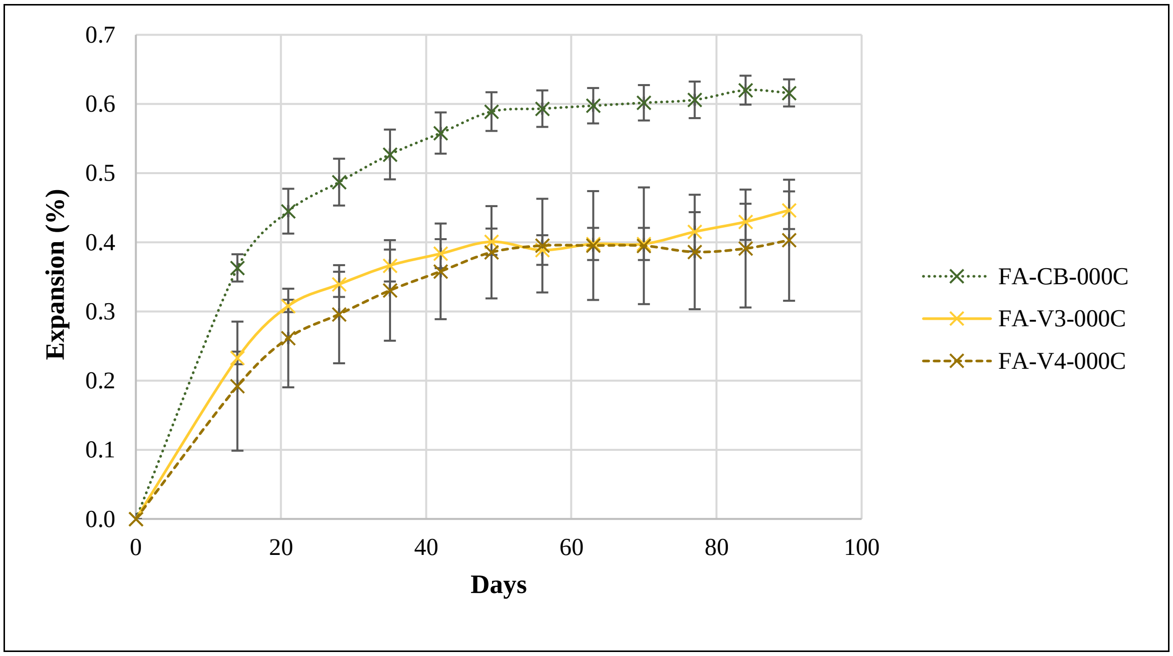

Figure 4.4 Average expansion of mini-bars versus time in control pastes.

Figure 4.5 presents the expansion of the pastes with the different percentages of CNTs. It is important to highlight that the vertical axis has a different scale than that of **Figure 4.4**. **Figure 4.5** shows a maximum expansion of 0.06%, which is 10 times less than that of the control pastes. This behavior can be explained by the fact that CNTs contribute mechanically as reinforcement in the cementitious material matrix. In addition, when CNTs are incorporated into the paste, they work physically as fillers and reduce the permeability of the paste, thus preventing the penetration of external agents and minimizing paste expansion; this behavior has been reported by other authors (Makar et al., 2005). In addition, CNTs promote a nucleation effect that generates a denser HAFAP microstructure; this effect will be explained in section 4.4.5 using SEM images.

Figure 4.5 shows that some samples could not reach the end of the test. This breakdown of the mixtures can be attributed to the incorporation of CNTs into the pastes, which generates a brittle material and causes the samples to break when small deformations occur; this behavior has also been reported by other authors (Mann, 2006). However, the brittle behavior was not observed in FA-CB, and all samples were able to reach the end of the test. In this case, the low calcium content allowed the generation of reaction products that, in turn, allowed a higher expansion and a more ductile material. These reaction products will be analyzed in sections 4.4.5, 4.4.6 and 4.4.7.

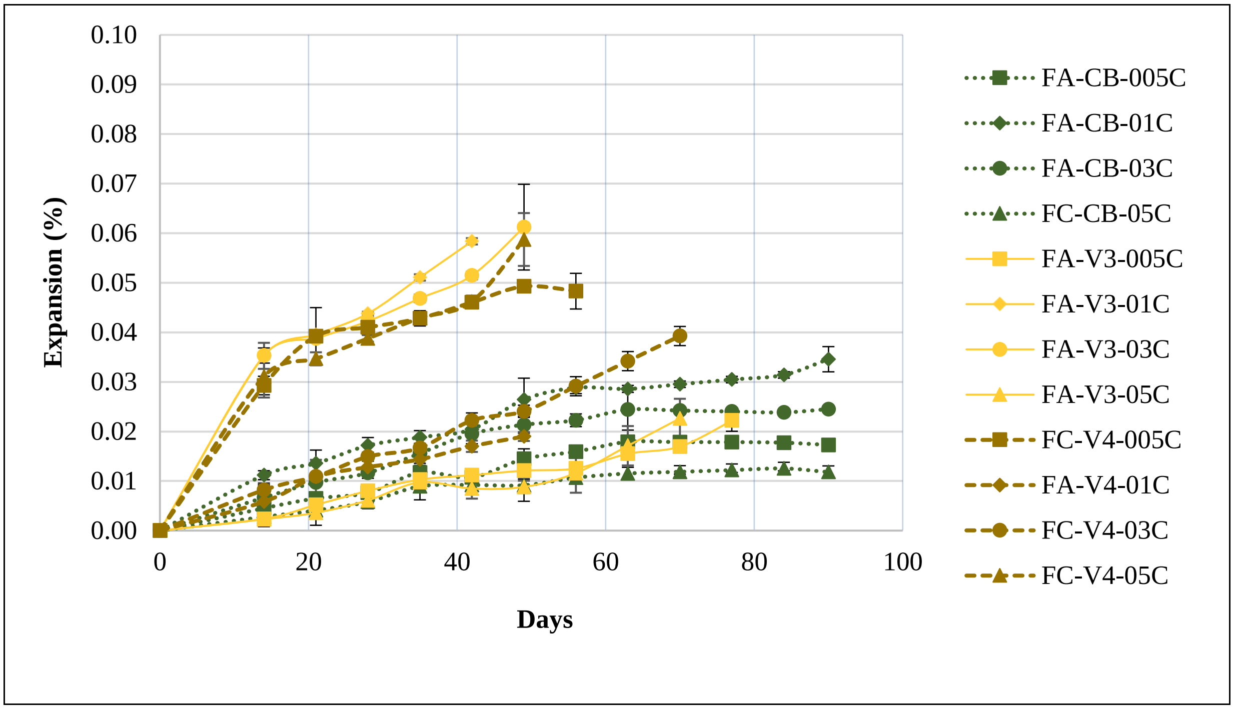

Figure 4.5 Average expansion of mini-bars versus time in pastes with CNTs.

Figure 4.6 presents the expansion results when functionalized CNTs (FCNTs) were incorporated into the mixture, and **Figure 4.6** shows a similar behavior obtained in mixtures with CNTs. However, when FCNTs were used in the same mixes, more samples were able to reach the end of the test. This behavior can be explained by the carboxyl group enhancing the bond of FCNTs with the reaction products and the ductility of the material; a similar behavior has been reported by other authors in pastes with 100% Portland cement (G. Y. Li et al., 2005).

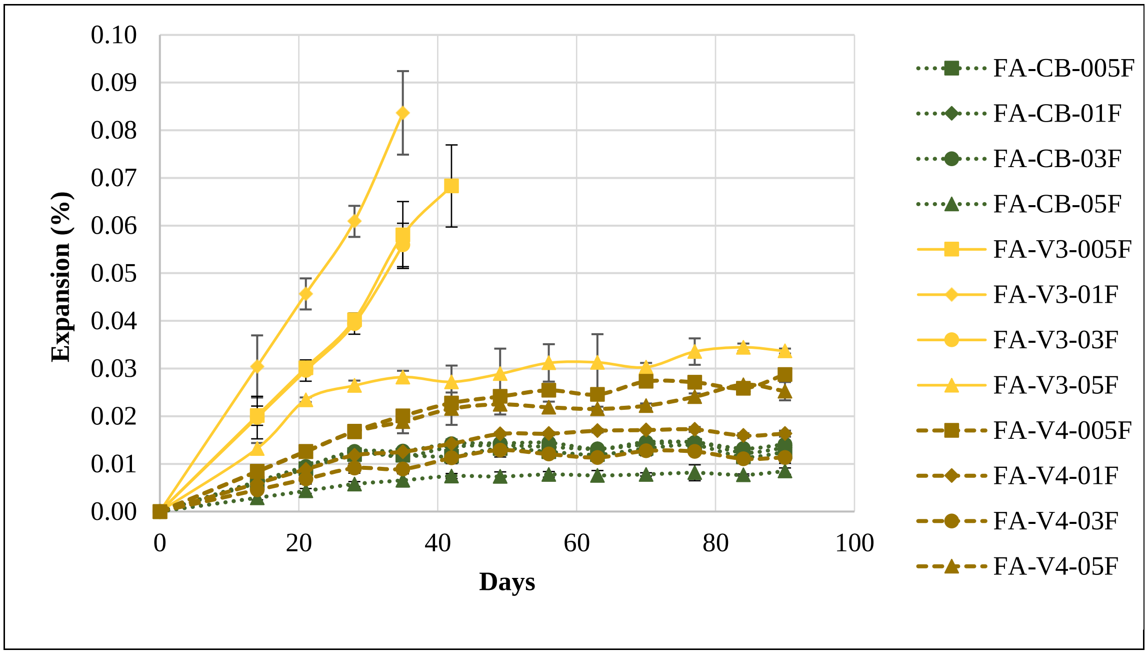

Figure 4.6 Average expansion of mini-bars versus time in pastes with FCNTs.

4.4.4 Compressive Strength

Figure 4.7 shows the compressive strength of the pastes with CNTs at 28, 56, and 90 days. From **Figure 4.7**, it is possible to determine that the incorporation of CNTs increases the compressive strength of the materials. This enhancement is explained by the physical contribution of CNTs, since they can act as filler material between the reaction products of the paste, either between calcium-silicate-hydrate (C-S-H) or between sodium-silicate-hydrate (N-A-S-H), common elements present in fly ash pastes that provide the hardening property of this material (Inés García-Lodeiro, Maltseva, Palomo, & Fernández-Jiménez, 2012). The nucleation effect also generates high-strength reaction products. Chemical and physical analysis is explained in more detail in sections 3.5, 3.6 and 3.7.

Figure 4.7 shows that the best behavior is obtained in the mix FA-V4; in the same paste, it should be noted that the best resistance is higher with 0.005% content of CNTs and then decreases as the percentage of CNTs increases.

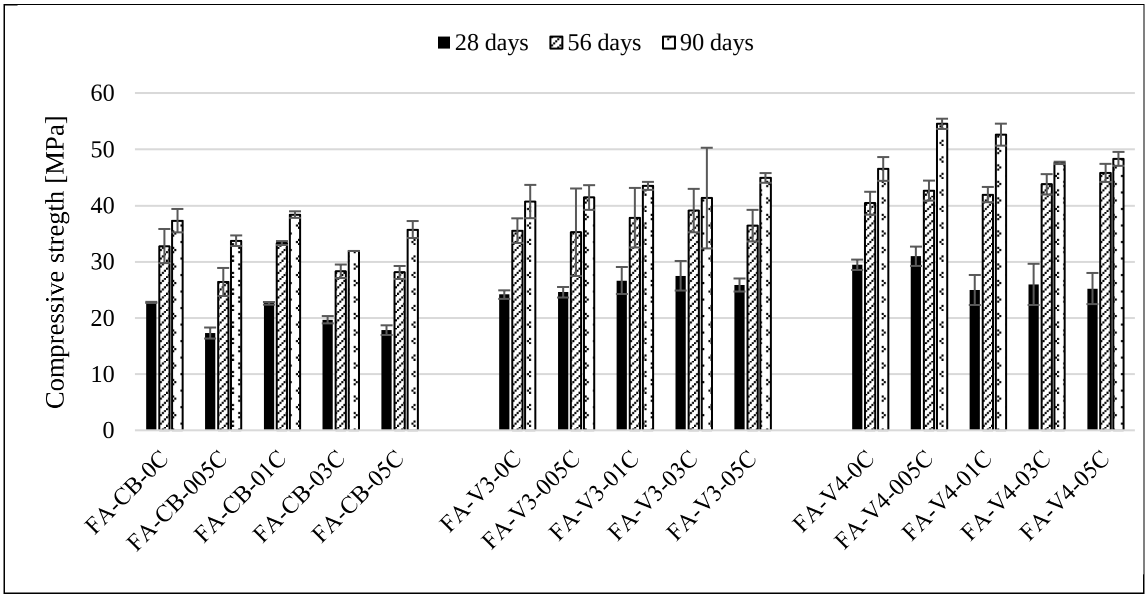

Figure 4.7 Compressive strength values for HAFAPs with conventional CNTs.

Figure 4.8 shows the compressive strength of the pastes with FCNT at 28, 56, and 90 days. From **Figure 4.8** it is possible to observe a similar trend compared with CNTs because the best behavior is obtained with FA-V4. However, with FCNTs, the compressive strength increases when the amount of FCNT increases; this behavior may be explained by the better interaction of FCNT with the reaction products.

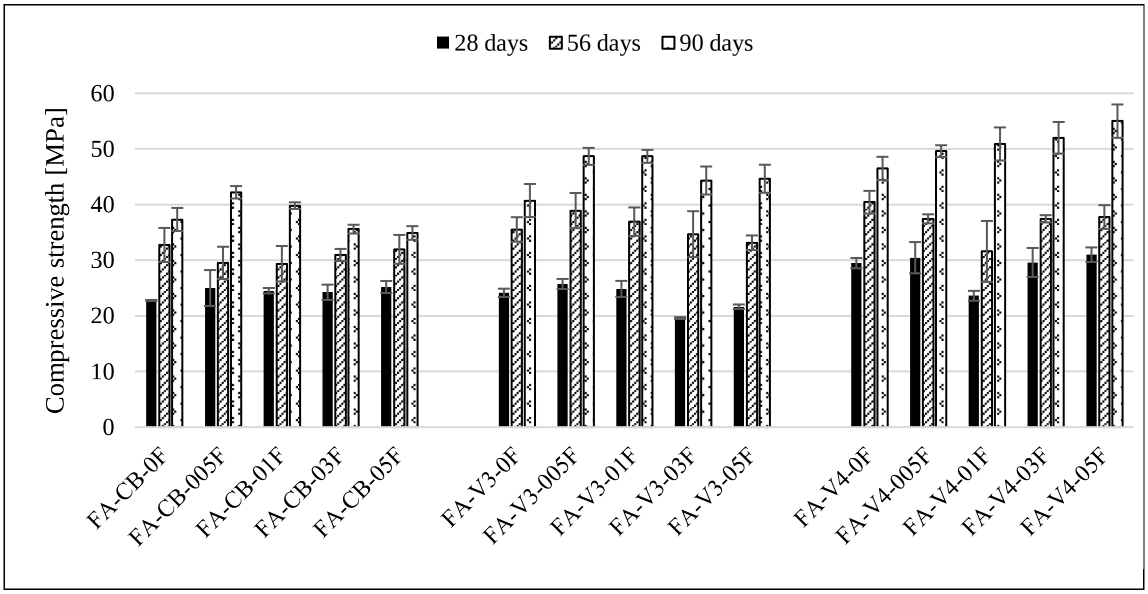

Figure 4.8 Compressive stregth values for HAFAPs with functionalized CNTs.

Figure 4.9 presents two representative pictures of test specimens for compressive strength and minibar tests of pastes that contain CNTs; both pictures were taken at 90 days. From the images, it is possble to observe that both specimens do not present any type of damage or distress on their surface. It is important to highlight that both samples were located in different exposure conditions; the compressive strengths were kept in a moisture room, whereas the minibar tests were kept in saturated conditions under exposure of sulfate attack.

Figure 4.9 Compressive strength and minibar specimens without damage on their surface at 90 days.

In order to complement the analysis of results and to thoroughly explain the behaviors in terms of expansion (i.e., the minibar test) and compressive strength, section 4.4.5 will present several results of the chemical and physical characterization of HAFAP microstructure. For simplicity, only the following pastes are analyzed in the next section: CB and V4 (both control pastes without CNTs), V4-005C, and V4-005F. These mixes were selected because of the results obtained in the compressive strength test and minibar test.

4.4.5 Field Emission Scanning Electron Microscopy with Energy-Dispersive X-Ray Spectroscopy (FESEM-EDX)

FESEM and EDX were carried out in the control HAFAPs, with CNTs and FCNTs with 0.005% (proportion of nanotubes). **Figure 4.10** shows the FESEM images for the HAFAPs; it is important to highlight that EDX analysis was performed in the full area covered by the image. These zones describe the morphology and chemical composition of hardened products. **Figure 4.10** shows the development of the geopolymerization of the reaction products in the control pastes of the cementitious matrix. The presence of N-A-

S-H and C-A-S-H was observed in the areas indicated in **Figure 4.10**, as reported by the EDX analysis. The results of the EDX analysis (see **Table 4.4**) indicate that the pastes with CNTs and FCNTs present a greater development of aluminosilicate and calcium silicate products when compared with the control pastes, CB and V4. Therefore, these results support the higher compressive strengths obtained at 90 days.

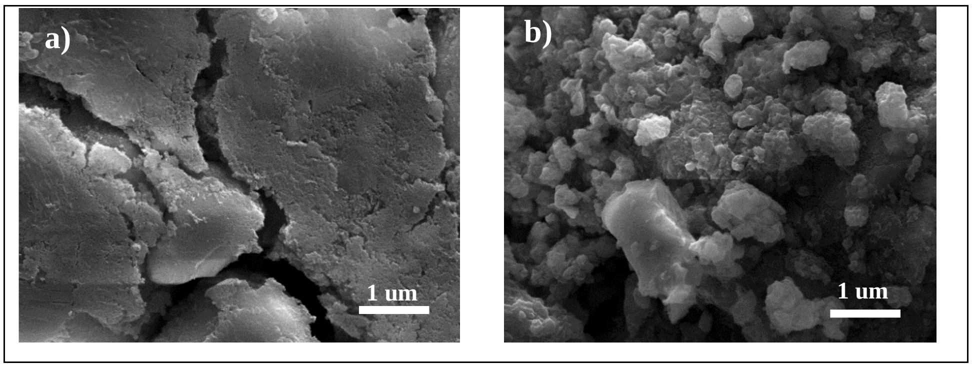

Figure 4.10 FESEM images of control pastes: (a) FA-CB and (b) FA-V4.

Table 4.4 EDX element analysis.

	Controls		**CNT**		**FCNT**	
Compound (%)	CB	V4	CB	V4	CB	V4
SiO_2	20.1	17.9	18.5	12.4	18.9	23.4
Al_2O_3	20.4	17.6	18.5	17.1	18.5	17.0
Na_2O	8.2	7.2	6.5	6.1	6.3	5.9
CaO	13.3	25.2	17.7	30.0	18.8	20.5
SO_4	22.8	21.0	20.9	26.1	20.0	21.0
SiO_2 + Al_2O_3 + CaO	62.0	68.0	61.1	65.6	62.5	65.5

Figure 4.11 presents FESEM images of the HAFAP microstructure with and without CNTs. The image with CNTs shows the bridge effect generated by the presence of carbon nanotubes; both CNTs and FCNTs may present the same behavior. This demonstrates the mechanical and physical effect of CNTs and FCNTs in HAFAPs.

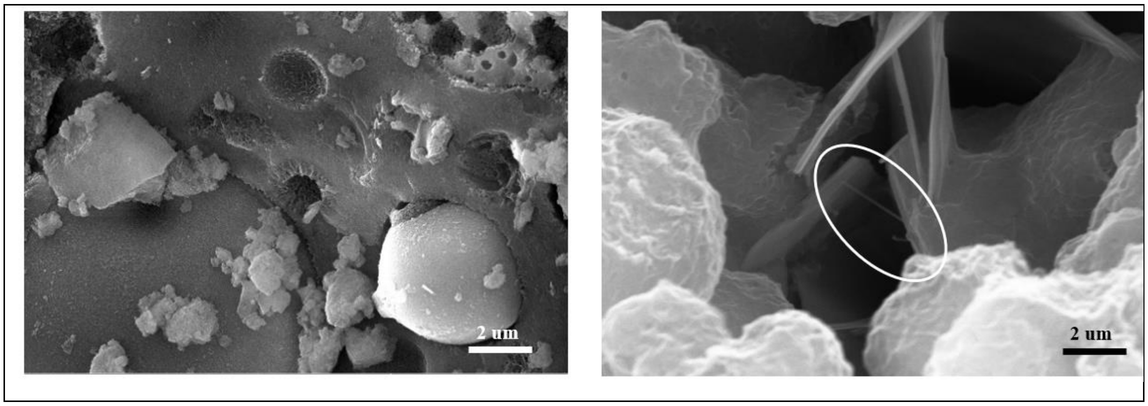

Figure 4.11 FESEM images of control pastes FA-CB and FA-CB with CNTs (on circle).

Furthermore, **Figure 4.12** presents a FESEM image that isolates a CNT. From **Figure 4.12** it is possible to observe the development of reaction products around the CNTs, which is known as nucleation. Although some authors have reported a similar behavior in Portland cement pastes (Makar et al., 2005; Tafesse & Kim, 2019), **Figure 4.12** reveals that the nucleation effect is also possible in HAFAPs. Both behaviors (bridge and nucleation effects) are novel results found in this type of material.

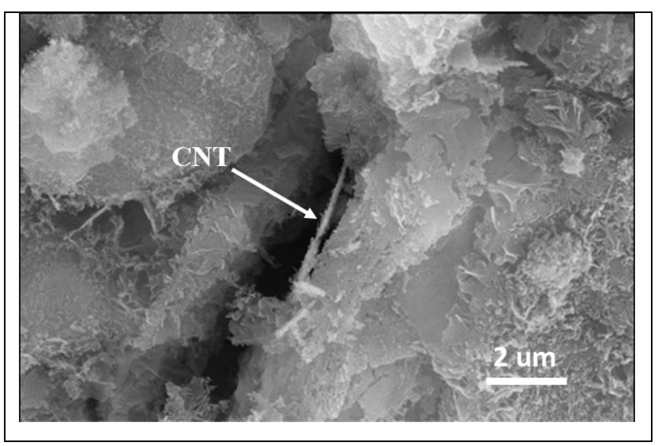

Figure 4.12 CNTs that present product development on their surface due to nucleation.

4.4.6 Fourier-transform infrared spectroscopy (FTIR)

FTIR was performed on the sample to understand their structure and the characteristics of reaction products. **Figure 4.13** shows the FTIR results of the samples at 90 days. The curves are from the control pastes (FA-CB and FA-V4), FA-V4-005C, and FA-V4-005F. The results indicate that the samples present their main absorption band between 970 and 1100 cm^{-1}, which is attributable to the combination of a N-A-S-H type gel and C-S-H (Ríos et al., 2020). This can be explained by the low amount of calcium present in FA-CB. It should also be noted that between 1100 and 1200 cm^{-1}, there is a small peak that can be identified as a state of vibration of SO_4 (Piqué & Vázquez, 2012), a component present in fly ash. In addition, between the absorption band of 850 and 960 cm^{-1}, there is a peak identified as C-A-S-H (Rea, Higuera, & Orozco, 2012). The FTIR analysis shows that the results are consistent with the EDX analysis and with the literature.

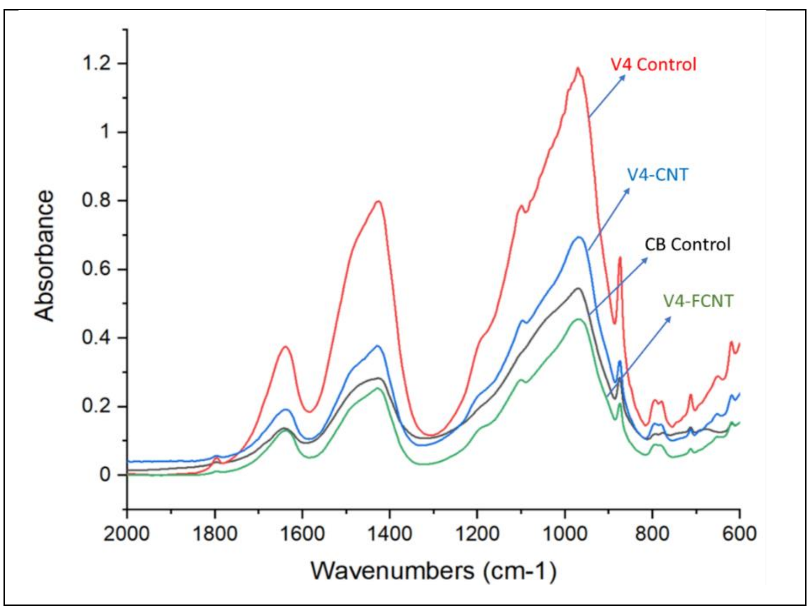

Figure 4.13 FTIR spectra for samples of the FA-CB and FA-V4 control and FA-V4 with CNTs and FCNTs at 90 days of curing.

4.4.7 X-ray diffraction (XRD)

Figure 4.14 shows the results of the X-ray diffraction analysis applied to the pastes at 90 days. According to the results obtained in this analysis, the presence of C_3S and gypsum was observed by the anhydrite cement and residual amounts of mullite and quartz from the hydrated paste. Also, due to the high content of sulfate in the fly ash, the presence of hannebachite was observed in the control paste FA-V4 (without carbon nanotubes). The results clearly indicate that there is no hannebachite in the pastes with CNTs and FCNTs, which explains their good performance with both types of nanomaterials. In addition to the physical contribution of CNTs and FCNTs in the pastes, the XRD results suggest that both nanomaterials (CNTs and FCNTs) chemically contribute to the pastes, reducing the harmful compound hannebachite. Furthermore, in the pastes with CNTs and FCNTs, a greater presence of ettringite and gypsum is observed. Given the characteristics of the samples, it was not possible to quantify the percentage of amorphous and crystalline content in the hybrid pastes.

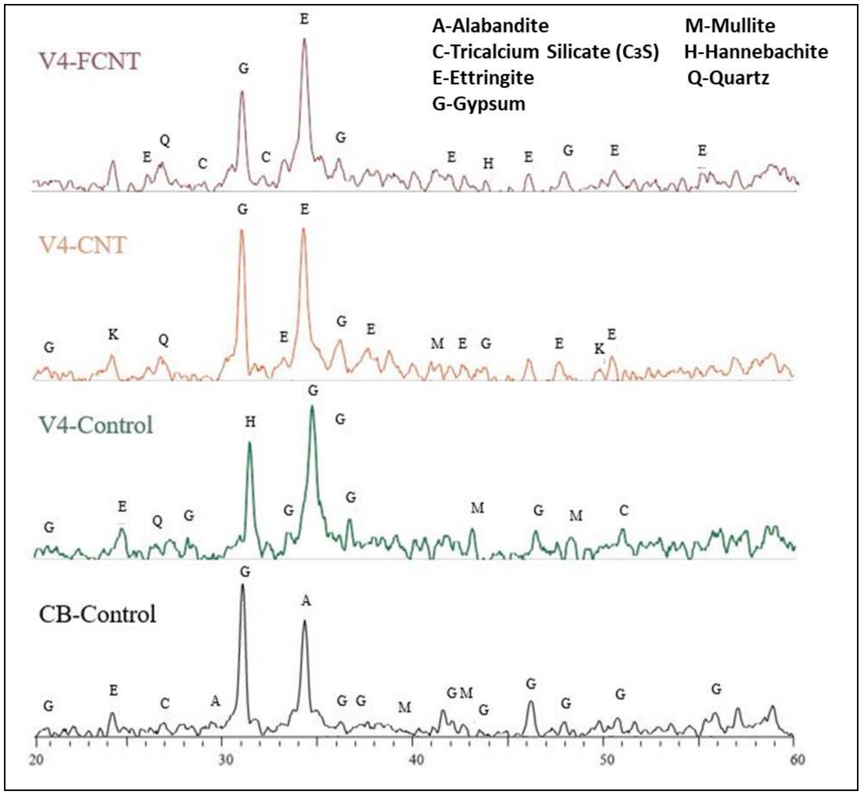

Figure 4.14 X-ray diffraction (XRD) patterns of HAFAPs with FA-CB, FA-V4 (control HAFAP), FA-V4 CNT, and FA-V4 FCNT at 90 days.

4.5 Conclusion

This article investigates the effects of incorporating conventional and functionalized CNTs in HAFAPs with a high amount of sulfate. The main conclusions obtained in this research are as follows:

- CNTs and FCNTs increase the compressive strength of HAFAPs in both the short and long term.
- The minibar test shows that CNTs and FCNTs improve the expansion resistance of mixtures. Furthermore, the mixtures are observed to be more brittle with the addition of CNTs.

- The FESEM observations reveal that the bridge and nucleation effects of carbon nanotubes also occur in the HAFAPs; this is a novel behavior not reported before in this type of material.
- The XRD results reveal that both types of nanotubes generate a chemical contribution to the paste quality because they do not promote formation of hannebachite, which is a harmful compound. This is also a novel behavior.
- The long-term performance of HAFAPs using marginal materials (fly ash with a high amount of sulfate) and CNTs was much better than in the control pastes. This means that CNTs are a promising alternative and promote the use of marginal materials that are currently discarded.
- CNTs did not present significant differences in chemical behavior compared to FCNTs. However, due to their surface treatment, the FCNTs showed better mechanical and physical behavior in the hybrid pastes.

The results of this research indicate that carbon nanotubes are a promising alternative to enhance the behavior of HAFAPs that incorporate fly ash with a high amount of sulfate. Thus, this circular economy approach can potentially reduce the use of cement and, in turn, CO_2 emissions worldwide.

4.6 Acknowledgements

Support funding for this research was provided by Comisión Nacional de Investigación Científica y Tecnológica de Chile (CONICYT) through the research project Fondecyt Iniciación 2017, number 11170157, and project Fondequip EQM150101. Also, the contribution of Dr. José Muñoz and Paulina Vergara to the results analysis is very much appreciated. Finally, authors acknowledge Colbun and AES Gener for the contribution with the fly ashes used in this research.

5. STATISTICAL ANALYSIS

Table 5.1 shows the statistical analysis of FA-CB, FA-V3 and FA-V4 samples for their control and the respective percentages of CNTs and FCNTs. This table shows the mean, standard deviation, and coefficient of variation of the compressive strength results at 90 days. The comparison in each mix was made taking in consideration the results of mixes without CNTs (0,0%) and the percentage that allows the higher compressive strength. Overall, the analyzed property presents a Coefficient of Variation (COV) of less than 10% which represent a suitable variability for this type of experiment.

Table 5.1 Mean, Standard deviation (SD), COV and p-value for pastes.

Type of Carbon Nanotube	Mix	Result of 90 days			
		Mean	SD	COV	p-value
Conventional	FA-CB-0C	37,3	2,31	6,19	0,507
	FA-CB-01C	38,33	0,58	1,51	
	FA-V3-0C	40,67	3,21	7,90	0,090
	FA-V3-05C	45,00	1,00	2,22	
	FA-V4-0C	46,67	2,52	5,39	0,007
	FA-V4-005C	54,67	1,15	2,11	
Functionalized	FA-CB-0F	37,33	2,31	6,19	0,031
	FA-CB-005F	42,17	1,10	2,61	
	FA-V3-0F	40,67	3,21	7,90	0,015
	FA-V3-01F	48,67	1,15	2,36	
	FA-V4-0F	46,67	2,52	5,39	0,021
	FA-V4-05F	55,00	3,00	5,45	

Figures 5.1 and 5.2 show the increase in compressive strengths of the pastes compared to the controls. With these results, an α- level hypothesis test was done for the compressive strengths to verify statistical differences. The assumed level of significance was α = 95%. In the analysis the null hypothesis test was $\mu = \mu_C$, where C correspond to the controls. The p-value was calculated in order to determine whether the compressive strength statistically different. If p-value > 0.05, the evidence is insufficient to reject the

null hypothesis and therefore $\mu = \mu_C$; otherwise, the null hypothesis must be rejected and hence $\mu \neq \mu_C$.

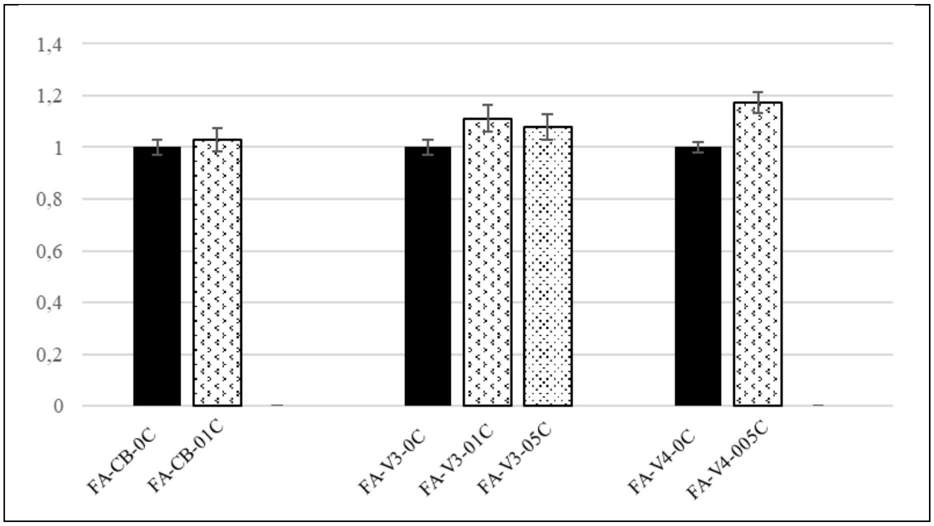

Figure 5.1 Statistical analysis for Fly ash pastes with CNTs.

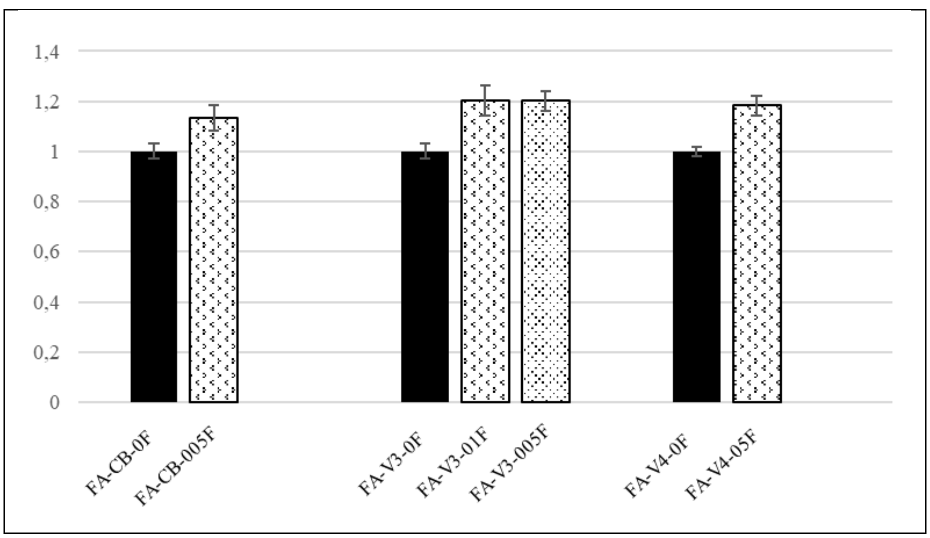

Figure 5.2 Statistical analysis for Fly ash pastes with FCNTs.

According to the previous analysis, it is possible to conclude that the following mixes present a significantly statistical difference: FA-V4-005C, FA-CB-005F, FA-V3-01F and FA-V4-05F. It is important to highlight that CNTs generate a statistically significant change in the FA-V4, in contrast, the FCNTs generate statistically significant changes in the all FA's.

Due to the big differences in the results obtained in the mini bar test between the mixes with and without CNTs and FCNTs, the hypothesis test was not performed. Since the differences are very big it is clear that exist a statistically significant modification between mixes.

6. CONCLUSIONS AND RECOMMENDATIONS

This research addresses the main physical and mechanical effects of the incorporation of conventional and functionalized nanotubes in hybrid alkaline activated Fly Ash pastes. According to the results, it was obtained that conventional and functionalized carbon nanotubes improves the compressive strength by 17% to 20%, this is due to the filling effect of the CNTs. In addition, they develop nucleation on the surface, achieving a greater amount of reaction products in the cementing matrix. Furthermore, it was found that the optimal amount of incorporation for the CNTs used is 0.005% after the sonication process.

Also, the addition of CNTs has decreased the expansion of the pastes subjected to sulfate attack by 10 times. It was observed that the pastes with conventional and functionalized CNTs show greater fragility and break after 45 and 40 days, respectively. This is due to the decrease of the pores in the hybrid paste and the potential use as reinforcement of the CNTs supporting the micro cracks.

Although the research shows promising results for the cementitious matrix and the CNTs used, it presents limitations of experimentation with other types of CNTs, with different functional groups that further improve the results already obtained. Besides, there is a limitation in the study of the relationship and interaction between the CNT and the dispersant material, in this case, the superplasticizer.

Furthermore, it is to possible to conclude from the statistical analysis that the incorporation of CNTs and FCNTs present strong statistical evidences that they generate significant changes in compressive strength compared with the control pastes.

Therefore, future research should focus on the interaction between the constituent materials, the chemistry between the polycarboxylate products such as the superplasticizer and its relationship with the functional groups, interaction between the reaction products such as NASH, CASH or CSH and functionalized CNTs. With this, the results already obtained in this first advance in the world of hybrid alkaline pastes could be improved.

Finally, throughout the investigation, different contributions to science have been generated, with successful results. The first of this was the article published in the journal "Construction and Building Materials" entitled "Assessing the effect of fly ash with a high SO_3 content in hybrid alkaline fly ash pastes (HAFAP)" in which the effects of fly ash with high sulfite content in alkaline hybrid pastes were studied.

In addition, a contribution was made to the article published in the same journal entitled "Assessing the bond strength of Glass Fiber Reinforced Polymer (GFRP) bars in Portland Cement Concrete fabricated with seawater through pullout tests" where the potential use of seawater in the manufacture of concrete with Glass Fiber Reinforced Polymer bars was studied as replacement of steel bars. In this investigation it was concluded that there is no statistically significant difference in the short-term bond strength (28 days) of GFRP bars in seawater concrete compared to normal concrete. It is important to highlight that this last article was achieved through a parallel collaboration during my Master program with the University of Ottawa through The Emerging Leaders in the Americas Program (ELAP).

REFERENCES

Alafogianni, P., Dassios, K., Farmaki, S., Antiohos, S. K., Matikas, T. E., & Barkoula, N. (2016). On the efficiency of UV – vis spectroscopy in assessing the dispersion quality in sonicated aqueous suspensions of carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *495*, 118–124. https://doi.org/10.1016/j.colsurfa.2016.01.053

Apparatus, A., & Inor-, O. (2020). Standard Specification for, 1–9. https://doi.org/10.1520/C0150

Ashby, M., Ferreira, P., & Schodek, D. (2009). *Nanomaterials, Nanotechnologies and Design*.

ASOCEM. (2018). Panorama mundial de la industria del cemento, 10. Retrieved from http://www.asocem.org.pe/archivo/files/Vision General de la Industria del Cemento y sus Principales Actores.pdf

ASTM, C. C. (2020). Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use, 1–5. https://doi.org/10.1520/C0618-19.2

Bigham, J. M., Kost, D. A., Stehouwer, R. C., Beeghly, J. H., Fowler, R., Traina, S. J., … Dick, W. A. (2005). Mineralogical and engineering characteristics of dry flue gas desulfurization products, *84*, 1839–1848. https://doi.org/10.1016/j.fuel.2005.03.018

Bouzoubaâ, N., Zhang, M. ., & Malhotra, V. . (2001). Mechanical properties and durability of concrete made with high-volume fly ash blended cements using a coarse fly ash. *Cement and Concrete Research*, *31*(10), 1393–1402. https://doi.org/10.1016/S0008-8846(01)00592-0

Chaipanich, A., Nochaiya, T., Wongkeo, W., & Torkittikul, P. (2010). Compressive strength and microstructure of carbon nanotubes – fly ash cement composites, *527*, 1063–1067. https://doi.org/10.1016/j.msea.2009.09.039

Chaipanich, A., Nochaiya, T., Wongkeo, W., Torkittikul, P., Ríos, A., González, M., … Kim, H. (2018). Graphene oxide prepared from mechanically milled graphite : Effect on strength of novel fly-ash based cementitious matrix. *Construction and Building Materials*, *177*(March), 10–22. https://doi.org/10.1016/j.conbuildmat.2018.05.051

Córdoba, P. (2015). Status of Flue Gas Desulphurisation (FGD) systems from coal-fired power plants : Overview of the physic-chemical control processes of wet limestone FGDs, *144*, 274–286. https://doi.org/10.1016/j.fuel.2014.12.065

Fernández-Jiménez, A., & Palomo, A. (2003). Characterisation of fly ashes. Potential reactivity as alkaline cements. *Fuel*, *82*(18), 2259–2265. https://doi.org/10.1016/S0016-2361(03)00194-7

Ferone, C., Colangelo, F., Messina, F., Iucolano, F., Liguori, B., & Cioffi, R. (2013). Coal combustion wastes reuse in low energy artificial aggregates manufacturing. *Materials*, *6*(11), 5000–5015. https://doi.org/10.3390/ma6115000

Ferraris, C., Stutzman, P., Peltz, M., & Winpigler, J. (2005). Developing a More Rapid Test to Assess Sulfate Resistance of Hydraulic Cements, *110*(5), 529–540.

Foldyna, J., Foldyna, V., & Zelenak, M. (2016). Dispersion of carbon nanotubes for application in cement composites, *149*(June), 94–99. https://doi.org/10.1016/j.proeng.2016.06.643

Fu, C., Ye, H., Zhu, K., Fang, D., & Zhou, J. (2020). Alkali cation effects on chloride binding of alkali-activated fly ash and metakaolin geopolymers. *Cement and Concrete Composites*, 103721. https://doi.org/10.1016/j.cemconcomp.2020.103721

García-Lodeiro, Ines, Fernández-Jiménez, A., Blanco, M. T., & Palomo, A. (2008). FTIR study of the sol-gel synthesis of cementitious gels: C-S-H and N-A-S-H. *Journal of Sol-Gel Science and Technology*, *45*(1), 63–72. https://doi.org/10.1007/s10971-007-1643-6

García-Lodeiro, Inés, Maltseva, O., Palomo, Á., & Fernández-Jiménez, A. (2012). Hybrid alkaline cements. Part I: Fundamentals. *Revista Romana de Materiale/ Romanian Journal of Materials*, *42*(4), 330–335.

García Lodeiro, I., Donatello, S., Fernandez-Jimenez, A., & Palomo, A. (2016). Hydration of Hybrid Alkaline Cement Containing a Very Large Proportion of Fly Ash : A Descriptive Model. https://doi.org/10.3390/ma9070605

Gartner, E. (2004). Industrially interesting approaches to “low-CO2” cements. *Cement and Concrete Research*, *34*(9), 1489–1498. https://doi.org/10.1016/j.cemconres.2004.01.021

He, Z., Zhu, X., Wang, J., Mu, M., & Wang, Y. (2019). Comparison of CO 2 emissions from OPC and recycled cement production. *Construction and Building Materials*, *211*, 965–973. https://doi.org/10.1016/j.conbuildmat.2019.03.289

Hielscher, T. (2005). Ultrasonic production of Nano-size dispersions and emulsions, (December), 14–16.

Keun, Y., Hwa, S., & Cheol, Y. (2019). Effects of chemical composition of fly ash on compressive strength of fly ash cement mortar. *Construction and Building Materials*, *204*, 255–264. https://doi.org/10.1016/j.conbuildmat.2019.01.208

Khan, N. N., & Sarker, P. K. (2020). Effect of waste glass fine aggregate on the strength , durability and high temperature resistance of alkali-activated fly ash and GGBFS blended mortar. *Construction and Building Materials*, *263*, 120177. https://doi.org/10.1016/j.conbuildmat.2020.120177

Kim, G. M., Nam, I. W., Yang, B., Yoon, H. N., Lee, H. K., & Park, S. (2019). Carbon nanotube (CNT) incorporated cementitious composites for functional construction materials : The state of the art. *Composite Structures*, *227*(February), 111244. https://doi.org/10.1016/j.compstruct.2019.111244

Kim, G. M., Nam, I. W., Yoon, H. N., & Lee, H. K. (2018). E ff ect of superplasticizer type and siliceous materials on the dispersion of carbon nanotube in cementitious composites. *Composite Structures*, *185*(October 2017), 264–272. https://doi.org/10.1016/j.compstruct.2017.11.011

Konsta-Gdoutos, M. S., & Aza, C. A. (2014). Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures. *Cement and Concrete Composites*, *53*. https://doi.org/10.1016/j.cemconcomp.2014.07.003

Li, G. Y., Ming, P., & Zhao, X. (2005). Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes, *43*, 1239–1245. https://doi.org/10.1016/j.carbon.2004.12.017

Li, Z., Lu, T., Liang, X., Dong, H., & Ye, G. (2020). Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes. *Cement and Concrete Research*, *135*(May), 106107. https://doi.org/10.1016/j.cemconres.2020.106107

Ma, P., Siddiqui, N. A., Marom, G., & Kim, J. (2010). Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites : A review. *Composites Part A*, *41*(10), 1345–1367. https://doi.org/10.1016/j.compositesa.2010.07.003

Makar, J., Margenson, J., & Luh, J. (2005). Carbon Nanotube/cement composites - Early Results and Potencial Applications. *3rd International Conference on Construction Materials*, *104*(March), 1682–1692. https://doi.org/10.1016/j.compositesb.2019.04.004

Malhotra, V. M., & Ramezanianpour, A. A. (1994). *Fly Ash in Concrete* (second). Ottawa: CANMET.

Mann. (2006). Nanotechnology and Construction. *Institute of Nanotechnology European Nanotechnology Gateway*, (November), 2–56.

Manzur, T., Yazdani, N., & Emon, A. B. (2016). Potential of Carbon Nanotube Reinforced Cement Composites as Concrete Repair Material, *2016*.

Mastali, M., Alzaza, A., Shaad, K. M., Kinnunen, P., Abdollahnejad, Z., Woof, B., & Illikainen, M. (2019). Using carbonated BOF slag aggregates in alkali-activated concretes. *Materials*, *12*(8). https://doi.org/10.3390/ma12081288

Mehta, P. K., & Gjørv, O. . (1982). Properties of portland cement concrete containing fly ash and condensed silica-fume. *Cement and Concrete Research*, *12*(5), 587–595.

Mehta, P. Kumar. (2004). *High Performance, High Volume Fly Ash Concrete For Sustainable Development*. *International Workshop on Sustainable Development and Concrete Technology*.

Mena, J., González, M., Remesar, J. C., & Lopez, M. (2020). Developing a very high-strength low-CO2 cementitious matrix based on a multi-binder approach for structural lightweight aggregate concrete. *Construction and Building Materials*, *234*, 117830. https://doi.org/10.1016/j.conbuildmat.2019.117830

Mendoza, O., Sierra, G., & Tobón, J. I. (2013). Influence of super plasticizer and Ca (OH) 2 on the stability of functionalized multi-walled carbon nanotubes dispersions for cement composites applications, *47*, 771–778. https://doi.org/10.1016/j.conbuildmat.2013.05.100

Moghaddam, F., Sirivivatnanon, V., & Vessalas, K. (2019). Case Studies in Construction Materials The effect of fl y ash fi neness on heat of hydration , microstructure , fl ow and compressive strength of blended cement pastes. *Case Studies in Construction Materials*, (2018), e00218. https://doi.org/10.1016/j.cscm.2019.e00218

Mohammed, T. U., Hamada, H., & Yamaji, T. (2004). Performance of seawater-mixed concrete in the tidal environment, *34*(September 2003), 593–601. https://doi.org/10.1016/j.cemconres.2003.09.020

Nagaraj, V. K., & Babu, D. L. V. (2018). Assessing the performance of molarity and alkaline activator ratio on engineering properties of self-compacting alkaline activated concrete at ambient temperature. *Journal of Building Engineering*, *20*(July), 137–155. https://doi.org/10.1016/j.jobe.2018.07.005

Oss, B. H. G. Van, Norton, G. A., & Survey, U. S. G. (2005). Background Facts and Issues Concerning Cement and Cement Data U . S . Department of the Interior.

Palomo, A. (2013). Cement & Concrete Composites Hydration kinetics in hybrid binders : Early reaction stages. *Cement and Concrete Composites*, *39*, 82–92. https://doi.org/10.1016/j.cemconcomp.2013.03.025

Palomo, A. (2014). *An overview of the chemistry of alkali-activated cement-based binders*. *Handbook of Alkaliactivated Cements, Mortars and Concretes*. Woodhead Publishing Limited. https://doi.org/10.1533/9781782422884.1.19

Piqué, T., & Vázquez, A. (2012). USO DE ESPECTROSCOPÍA INFRARROJA CON TRANSFORMADA DE FOURIER (FTIR) EN EL ESTUDIO DE LA HIDRATACION DEL CEMENTO.

Qi, W., Liu, J., & Leung, F. (2019). A framework to quantify impacts of elevated CO 2 concentration , global warming and leaf area changes on seasonal variations of water resources on a river basin scale. *Journal of Hydrology*, *570*(January), 508–522. https://doi.org/10.1016/j.jhydrol.2019.01.015

Rashad, A. M. (2015). A brief on high-volume Class F fly ash as cement replacement – A guide for Civil Engineer. *International Journal of Sustainable Built Environment*. https://doi.org/10.1016/j.ijsbe.2015.10.002

Rea, S. P. A., Higuera, R. C., & Orozco, V. M. (2012). Caracterización de cenizas volantes activadas alcalinamente como material alternativo al cemento, 77–84.

Ríos, A., González, M., Montes, C., Vásquez, J., & Arellano, J. (2020). Assessing the effect of fly ash with a high SO 3 content in hybrid alkaline fly ash pastes (HAFAPs), *238*. https://doi.org/10.1016/j.conbuildmat.2019.117776

Safiuddin, M., Gonzalez, M., Cao, J., & Tighe, S. L. (2014). State-of-the-art report on use of nano-materials in concrete. *International Journal of Pavement Engineering*, *15*(10), 940–949. https://doi.org/10.1080/10298436.2014.893327

Salavagione, H. (2011). Funcionalización de nanotubos de carbono y grafeno con polímeros mediante química click, (January).

Scrivener, K. L., John, V. M., & Gartner, E. M. (2018). Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry. *Cement and Concrete Research*, *114*(June), 2–26. https://doi.org/10.1016/j.cemconres.2018.03.015

Shah, S. P., Hou, P., & Konsta-Gdoutos, M. S. (2015). Nano-modification of cementitious material: Toward a stronger and durable concrete. *Journal of Sustainable Cement-Based Materials*, *5*(1). https://doi.org/10.1080/21650373.2015.1086286

Sharma, S., Susan, D., Kothiyal, N. C., & Kaur, R. (2018). Graphene oxide prepared from mechanically milled graphite : Effect on strength of novel fly-ash based cementitious matrix. *Construction and Building Materials*, *177*, 10–22. https://doi.org/10.1016/j.conbuildmat.2018.05.051

Shi, C., Jiménez, A. F., & Palomo, A. (2011). Cement and Concrete Research New cements for the 21st century : The pursuit of an alternative to Portland cement. *Cement and Concrete Research*, *41*(7), 750–763. https://doi.org/10.1016/j.cemconres.2011.03.016

Siddique, R. (2004). Performance characteristics of high-volume Class F fly ash concrete. *Cement and Concrete Research*, *34*(3), 487–493. https://doi.org/10.1016/j.cemconres.2003.09.002

Siddique, R. (2010). Utilization of coal combustion by-products in sustainable construction materials. *Resources, Conservation and Recycling*, *54*(12), 1060–1066. https://doi.org/10.1016/j.resconrec.2010.06.011

Tafesse, M., & Kim, H. (2019). The role of carbon nanotube on hydration kinetics and shrinkage of cement composite. *Composites Part B*, *169*(March), 55–64. https://doi.org/10.1016/j.compositesb.2019.04.004

Worrell, E., Price, L., Martin, N., Hendriks, C., & Meida, L. O. (2001). Missions from ∗ the. *Carbon*, *26*, 303–329. https://doi.org/10.1146/annurev.energy.26.1.303

Yu, J., Grossiord, N., Koning, C. E., & Loos, J. (2007). Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution, *45*, 618–623. https://doi.org/10.1016/j.carbon.2006.10.010

Zhang, Z., Provis, J., Ma, X., Reid, A., & Wang, H. (2018). Efflorescence and subflorescence induced microstructural and mechanical evolution in fly ash-based geopolymers.

Zunino, F., Bentz, D. P., & Castro, J. (2018). Reducing setting time of blended cement paste containing high-SO 3 fl y ash (HSFA) using chemical / physical accelerators and by fl y ash pre- washing. *Cement and Concrete Composites*, *90*, 14–26. https://doi.org/10.1016/j.cemconcomp.2018.03.018