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Use of alternative materials in soil stabilization: mechanical and environmental aspects

Hani Baloochi

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Use of alternative materials in soil stabilization: mechanical and environmental aspects

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WHITE PAGE

USE OF ALTERNATIVE MATERIALS IN SOIL STABILIZATION: MECHANICAL AND ENVIRONMENTAL ASPECTS

Doctoral Thesis submitted in fulfilment of the requirements for the
Degree of Doctor of Philosophy in Construction Engineering

by

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Abstract

Currently, the two most raw material consumer industries are civil engineering and the pulp and paper industry. Meanwhile, these sectors face severe criticism due to their environmental impact. Additionally, by increasing more strict regulations over the disposal of pulp and paper waste into landfills, European unions are looking for the possible use of different applications of paper ash.

This doctoral thesis is a part of the European Union project (Paperchain), which has the participation of 20 European partners (Spain, Portugal, Sweden, Slovenia, and France), which include construction companies, paper companies, research centres, and universities.

This thesis aims to study the possibility of using waste paper fly (WPFA) and bottom ash (WPBA), which come from a recycled paper plant (energy recovery plant) in Spain. The goal is to use WPFA and WPBA as cementing materials to stabilize soil without incorporating any other traditional binder material. Therefore, an in-depth characterization of the two types of ashes (WPFA and WPBA) is carried out to determine their hydration process and strength gain. Also, when ashes are mixed with soils for stabilization, different amounts of binder, water and delay times for compaction of the samples are studied.

Determining the environmental impact of WPA is an essential step to the safe use of WPA as binders. Hence, in the first place, the chemical, mineralogical, and size distribution of WPA during one year of sample collecting from the recycling paper plant was conducted. Then, release of pollutants from stabilised soils with WPFA is also studied by means of leaching test in the laboratory and the trial field.

Cement and lime are prone to swell when becoming in contact with a sulfate source. Owing to similarities between the cement and WPA, the stabilized soil was placed in contact with different sulfate concentrations to determine the swelling and to assure its safe use. Finally, as most of the experiments were conducted in the laboratory, field experimental sections were carried out to verify the performance of stabilised soils with ashes.

The chemical and mineralogical variation during the one-year sample collection from the paper plant demonstrated little changes in WPFA and WPBA. Hydration in both ashes is similar, when mixed with water, hydrated calcium silicates gel (C–S–H), portlandite and, in some cases, Friedel's salt are generated. This process is slower in bottom ash (WPBA) and therefore its mechanical performance is lower compared to fly ash (WPFA).

The amount of water plays an important role in swelling and the final strength of stabilised soil. To achieve better workability and minimise swelling it is important to add 30-minute delay time after mixing soil, ash and water. In addition, to obtain the greatest workability, reducing the water content by one point of Proctor value improved the strength significantly. In relation to durability results, different sulfate concentrations and temperatures had no effect on the durability of stabilized soil with WPFA. At long ages formation of ettringite is observe, in very low quantities, possibly due to the consumption of all aluminium in the system.

The environmental impact assessment of WPA showed stabilized soil can be categorized as inert material. However, it should be mentioned that WPFA solely released a high amount of barium (Ba). Environmental test carried out on the experimental field trial do not show any negative effects in the environment.

Finally, from a mechanical, environmental, and durability standpoint it has been successfully demonstrated that the implementation of WPFA as the sole hydraulic binder is possible.

Keywords: Waste paper ash, environmental impact, cementitious material, Portland cement, soil, stabilised soil, sulphate attack, swelling, compressive strength.

Resumen

En la actualidad, las dos industrias con mayor demanda de materias primas son la ingeniería civil y la industria de la pasta y el papel. Al mismo tiempo, estos sectores se enfrentan a fuertes criticas debido al impacto ambiental que generan. Adicionalmente, debido al incremento en regulaciones más restrictivas sobre la disposición de los residuos de la pulpa y el papel en vertederos, la Unión Europea está buscando salidas al posible uso, en diferentes aplicaciones, de este tipo de residuos.

Esta tesis doctoral se enmarca dentro del proyecto europeo PaperChain, en el cual participan más de 20 socios europeos (España, Portugal, Suecia, Eslovenia y Francia), entre los que se encuentran empresas del sector de la construcción, empresas papeleras, centros de investigación y universidades.

Esta tesis se propone estudiar la posibilidad de utilizar las cenizas volantes (WPFA por sus siglas en ingles) y de fondo (WPBA) provenientes de la quema de residuos de papel en una planta de valorización energética. El objetivo es utilizar las cenizas volantes y de fondo como materiales cementantes para estabilizar suelos sin incorporación adicional de ningún otro cementante tradicional. En este sentido, se realiza una caracterización profunda de los dos tipos de cenizas (WPFA y WPBA) para determinar su proceso de hidratación y ganancia de resistencia. Cuando se mezclan con suelos, para su estabilización, se estudian diferentes cantidades de aglomerante, agua y tiempos de retraso para la compactación de las muestras.

La determinación del impacto ambiental de las cenizas es un paso esencial para el uso seguro de este residuo como aglomerante. Por lo tanto, en primer lugar, se llevo a cabo un análisis de la composición química, mineralógica y distribución de tamaño de partícula de las cenizas, durante un año. También se estudia la liberación de contaminantes, por medio de ensayos de lixiviación, de suelos estabilizados con cenizas tanto en laboratorio como en campo.

El cemento Portland y la cal, utilizados en la estabilización de suelos, son propensos a expandir cuando entran en contacto con una fuente se sulfatos. Debido a las similitudes entre el cemento y las cenizas (WPA), el suelo estabilizado con estos materiales se puso en contacto con diferentes concentraciones de sulfato para medir la expansión y conocer la posible expansión generada y, así, garantizar su uso seguro. Finalmente, como la mayoría de los experimentos se realizaron en el laboratorio, se realizaron tramos experimentales de campo para verificar el desempeño de las cenizas.

La variabilidad química y mineralógica de las muestras recogidas durante un año mostró que hay pocos cambios en las cenizas volantes (WPFA), como en las cenizas de fondo (WPBA). La hidratación en los dos tipos de cenizas es similar, cuando se mezclan con agua, se generan silicatos de calcio hidratados (SCH), portlandita y, en algunos casos, sal de Friedel. Este proceso es más lento en las cenizas de fondo (WPBA) y por lo tanto su desempeño mecánico es menor en comparación con las cenizas volantes (WPFA).

La cantidad de agua juega un papel importante en el hinchamiento inicial y en la resistencia final de los suelos estabilizados. Para lograr una mejor trabajabilidad y reducir al máximo el hinchamiento es importante añadir un tiempo de retraso de 30 minutos después de mezclar el suelo, las cenizas y el agua. Además, para obtener la mayor trabajabilidad, la reducción del contenido de agua en un punto del valor Proctor mejora significativamente la resistencia a compresión.

En relación a los resultados de durabilidad. las diferentes concentraciones de sulfato y temperaturas no tuvieron efecto en la expansión del suelo estabilizado con ceniza volantes (WPFA). A largas edades se observa la formación de etringita, en muy bajas cantidades, posiblemente por el consumo de todo el aluminio en el sistema.

El estudio de impacto ambiental del suelo estabilizado con cenizas volantes (WPFA) puede ser categorizado como material inerte. No obstante, se debe mencionar que las cenizas (WPFA) liberan una cantidad elevada de bario (Ba). Los ensayos ambientales realizados en el tramo experimental no muestran afectaciones negativas al entorno.

Finalmente, desde el punto de vista mecánico, de durabilidad e impacto ambiental se ha demostrado con éxito que la implementación de las cenizas (WPFA) como único aglomerante hidráulico es posible.

Palabras clave: Residuos de cenizas de papel, impacto ambiental, material cementante, cemento Portland, suelo, suelo estabilizado, ataque sulfático, expansión, resistencia a compresión.

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Contributions

This research has contributed to the field of construction engineering through different academic results: three scientific publications, presentations at congresses and conferences, and deliverables for one competitive project.

	Impact Factor	Quartile	Publisher
Chapter 3 Article 1 (published)	8.910	Q1	Journal of Environmental Management
Chapter 4 Article 2 (published)	2.838	Q2	MDPI Applied Sciences
Chapter 5 Article 3 (published)	3.748	Q2	MDPI Materials
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- Cepriá, JJ; Orejana, R; Miró, R; Martínez, A; Barra, M; Aponte, D; **Baloochi, H**. (2021). Waste paper ash as an alternative binder to improve the bearing capacity of road subgrades. 11th International Conference on the Bearing Capacity of Roads, Railways and Airfields.

Prizes

- World Road Association Prize 2019 for the Best Innovation.

Involvement in competitive projects

- New market niches for the Pulp and Paper Industry waste based on circular economy approaches (PaperChain project). H2020-730305-PAPERCHAIN.

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Chapter 1

1.1. Introduction

The ever-growing demand for natural resources in different sections is causing/caused resource scarcity. A sector that depends highly on exploiting natural resources is the civil engineering field. The annual consumption of this field as reported are 40% of stone, gravel and sand, 25% of virgin wood, 37-40% of total energy, and 16% of annual water [1–3]. Meanwhile concrete is the most widely used and cheap material, and cement is an essential element of concrete which accounts for 7% of global CO_2 emissions [4] and a production of 4.1 billion tonnes in 2019 as estimated by the European Cement Association [5]. Nowadays, there is an urge to find more environmentally friendly construction materials to overcome the depletion of natural resources while reducing the pollution produced during civil engineering sector. Numerous research works are carried out to find a new way to reduce the impact of civil engineering sector, from recycling/modifying the constituent of concrete like aggregates [6–10], adding other constituents such as admixtures [11–14], pigments, fibres [15–17], and polymers [18]. Moreover, significant amounts of research had been conducted to replace any constitute of concrete or cement by other waste/by-product materials such as Ground Granulated Blast-furnace Slag (GGBS) [19,20], fly ash [21–23], coal refuse from mining industry, municipal solid waste ash [24,25], red mud [26], rice husk ash [27,28].

Similarly, another sector that has been criticized over the past is pulp and paper industry. This sector besides being an energy-intensive sector [29], during manufacturing produces significant amount of waste, hence authorities are trying to decrease the environmental impact of this sector. Various waste such as ash, dregs, grits, lime mud, and pulp mill sludge from various treatment are produced [30]. According to CEPI, the pulp production/consumption was estimated 183 million tonnes in 2019. Moreover, the paper and board production were estimated around 412 million tonnes. Meanwhile, the recycling rate for paper was calculated at 74% in 2019 [31]. Despite the great effort of reaching this high rate of recycling, pulp and paper industries are still producing significant amount of organic and inorganic wastes. To reduce the amount of waste produced while producing electricity, fluidized bed combustion (FBC) is being used. The output of this process is two types of ash known as waste paper fly ash (WPFA) and waste paper bottom ash (WPFA). These wastes in the past used to end up in landfill, but nowadays, due to new regulations and restrictions, it is getting more difficult to dispose these wastes to the landfills.

In addition, Europe today faces the challenge of resource scarcity and more efficient use. If properly managed, waste from the paper industry can become a valuable raw material for other resource-intensive industries such as construction (5.4 billion tonnes of raw material consumption) or the chemical industry (1 billion tonnes). In addition, waste generation from the mining industry is estimated at 20 billion tonnes of solid waste per year.

The EC initiative "Roadmap to a Resource Efficient Europe" aims at more sustainable use of resources by transforming waste into resources by reusing raw materials through "industrial symbiosis". New widespread markets are needed to expand recovery operations, reduce landfill rates, and increase the competitiveness of companies by creating new value-added markets for their inorganic waste.

In the above context, the Europe PaperChain project “new market niches for the pulp and paper industry waste based on circular economy approaches” is being developed with the general aim of deploying five novel circular economy models centred on the valorisation of the waste streams generated by the Pulp and Paper Industry as secondary raw material for a number of the resource-intensive sector: construction sector, mining sector, and chemical industry. PaperChain aims to unlock the potential of a resource-efficient model based on industrial symbiosis, which will demonstrate the potential of the major non-hazardous waste streams generated by the pulp and paper industry as valuable secondary raw materials.

The PaperChain project follows a systemic approach for each of the main sectors it targets, integrating the entire value chain from waste production to final application. In each sector, all major stakeholders are present in the circular model, including waste production, waste treatment and recovery, product manufacturing, product end-users, and civil society. Thus, the project develops five different models, namely:

Construction sector

- **Circular Case 1**: valorisation of paper industry’s causticizing residuals (i.e., lime mud, slakers grits, green liquor dregs) as secondary raw materials for concrete and asphalt manufacturing.
- **Circular case 2**: valorisation of deinking paper sludge and waste paper ash produced by Recycling Pulp mills for the rehabilitation and slope stabilization of landslides in Railway lines.
- **Circular case 3**: valorisation of ash produced in the energy recovery from paper waste produced by Recycling Pulp mills as an alternative binder for soil stabilization works in road projects.

Chemical sector

- **Circular case 4**: valorisation of fibre sludge waste generated by the Pulp industry as secondary raw materials for the production of ethanol derivatives for the Chemical industry (i.e., paints).

Mining sector

- **Circular Case 5**: valorisation of green liquor dregs produced by the Pulp industry as reactive sealing layers for acid rock drainage mitigation in mine waste deposits.

In relation to the PaperChain project, this doctoral work focuses on the Circular case 3, which is based on research on the valorisation of waste paper ash for construction. It is therefore proposed to demonstrate the technical and environmental performance of the new binders in three pilot cases, from the less complex and more easily accessible to the market (rural roads), to the more complex and regulated (highways).

1.2. Objective

The general objective of this doctoral work is to study how to use waste paper ash, which are getting more common in many parts of the world, as a cementitious material in soil stabilisation. These ashes are intended to be used as the sole binder, totally replacing conventional binders such as lime or Portland cement, taking into consideration the mechanical, durability, and environmental aspects of their use.

In order to achieve the main objective, the specific objectives are as follows:

- To carry out a study of the physical, chemical and mineralogical properties of paper ash residues in order to determine their viability as an agglomerate for soil stabilisation. For this purpose, the hydration process of these ashes is studied, as well as the evolution of the mechanical resistance using standardised mortars. Finally, the environmental impact of the ashes is studied by means of leaching tests (Chapter 3).

- Use Waste Paper Fly Ash (WPFA) as the sole binder, totally replacing the cement Portland, to obtain a stabilised soil type 3 which includes 1.5 MPa in unconfined compressive strength. Furthermore, describing the precautions associated with WPFA and the implementation of its use as a stable binder in soil, to fulfil the requirement of Spanish guidelines - PG3: 2014 - (Chapter 4).

- To study the durability of the soil stabilised with WPFA. For this purpose, a long-term monitoring of a stabilised soil in presence of different sulphate concentrations is carried out by measuring mechanical performance and swelling. All tests were carried out in different conditions (at 5 ºC and 20 ºC), and the results were compared with a commonly used binder (CEM IV). Mineralogical changes were monitored using different techniques such as X Ray Diffraction (XRD), Thermo-

Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy Analysis (SEM) (Chapter 5).

- Based on the results obtained in the laboratory, using the paper ashes, make a compendium of the different types of stabilised soils made on a real scale showing the performance of the new materials in each case (Chapter 6).

1.3. Structure of the thesis

This thesis doctoral is structured as independent chapters that have been presented to peer-reviewers for their publication as scientific articles. The overall structure of this thesis is developed in four parts, where the first article tackles the utilisation of WPFA and WPBA as binder in different types of soils, while taking into consideration the environmental impact of these ashes. Article 2 introduces two precautions for correct use of WPFA as sole binder in soil. Article 3 is concerned with the durability of WPFA and comparing its finding to a pozzolanic cement. Finally, the book chapter examines the real-life scenario using WPFA as a binder replacing 100% of conventional cement. The summary of each chapter is given below:

Chapter 3 – Article 1

In the first article, an in dept characterization of both WPFA and WPBA is carried out. The characterization includes of physical, chemical properties, and mineralogical characteristics of WPFA and WPBA. To estimate the environmental threat, leaching tests have proven to be essential characterization tools, hence the environmental impact of these ashes also was studied. Respecting the mechanical behaviour, various soils were treated with these ashes to understand these ashes better.

Chapter 4 – Article 2

In this article, the objective was to deal with WPFA as sole binder in soil to satisfy the Spanish requirements for roads. Moreover, in the study a new way of measuring the expansion was introduced. Additionally, some precautions were introduced to make WPFA a suitable binder in soil stabilization.

Chapter 5 – Article 3

The objective of this article was to study the durability of WPFA as binder in comparison to a traditional binder (pozzolanic cement type IV). The study took into account the swelling effect of different sulfate concentrations and temperatures on the soil stabilized with WPFA. Moreover, the strength of soil treated with WPFA during a year was determined and compared to those with cement. Lastly, microstructural studies carried out to verify all the finding obtained from swelling and strength experiments.

Chapter 6 – Book chapter

The aim of this book chapter was to make a description of different types of stabilised soils using WPFA, which were carried out on real construction sites. These constructions sites represent a wide range of mechanical service conditions, ranging from low to high traffic. Preliminary laboratory tests are described, as well as quality control results during and after construction of the experimental sections.

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Chapter 2

2.1. Background

Europe is a major producer of pulp and paper, representing 25% of world production [1]. This sector produces a significant amount of waste yearly [2–4]. These wastes come from different part of paper manufacturing such as deinking, pulping processes, and wastewater treatment. In addition, managing waste, particularly industrial waste, is a concern for many nations, due to occupying a large amount of land, or affecting underground water quality [4]. Moreover, in some part of the Europe, disposal to landfill is being restricted. Consequently, a new answer is required to cope with waste management. One answer is the development of innovative systems to maximize the reusing waste materials in a sustainable and economical way. A potential sector is in construction owing to its vast size. Numerous studies are conducted to approach pulp and paper reutilization in different construction sector [5–10]. Recently, to reduce the amount of waste produced in pulp and paper industry, incineration is being used. A new and efficient technology is to use fluidized bed combustors (FBC). FBC provides more flexibility and to some extend lesser emissions. However, there is still some drawbacks to this system such as more investments, and formation of ashes at the end of process. These ashes are very diverse in composition. The diversity depends on the raw material used during incineration, and the temperature of combustion. Even so, there are some similarities between the ashes produced. Generally, ashes consist of some porous material and the main elements are calcium, aluminium and silicate [11–17]. Significant amount of research efforts has been dedicated to resolve the waste paper ash generated in paper industry. Gailius [18] tried to make an economic binder from waste paper sludge ash (WSA) and GGBS in concrete production without incorporating Portland cement. It was concluded that concrete with a mix of WSA and GGBS is possible. Additionally, the mix of WSA-GGBS showed a fast hydration in early ages between 1 to 7 days. Mozaffari [11] showed that owing to the high content of free lime in WSA, the porosity of WSA is also high, leading to low strength. Tom compensate for this expansion, Segui [17] introduced a 25 min delay time before adding the mortars made with WSA into the mold. The study continued with treating a clayey soil with a mixture of WSA and gypsum. The results indicated an acceptable strength for hydraulic roads, gained a high strength at 3 days, and formation of ettringite in soil samples. However, no expansion was observed. Another study demonstrated that paper sludge ash (PSA) showed a good strength even better than clay treated with lime or cement, in most cases. Additionally, it was concluded a better material with low environmental impact and more economic benefits [8]. However, it was found that WSA in combination with tartaric acid is not as good as Portland cement, still, the gained strengths were between 0.4 to 4.7 MPa for 8% to 14% WSA at 7 days, respectively [7].

In most cases WPA can achieve some degree of strength on its own. Therefore, it is better to use in cases where the strength is not high. One of the sectors that can benefits from WSA is soil stabilization. The most common stabilizers for soil are cement and lime, which have shown a negative impact on environment. Soil stabilization with a WSA, not only reduces the CO_2 emissions produced by cement industry, but also eliminates the landfill problems facing WSA. However, two significant aspects that should be considered regarding the use of WSA as binder in soil stabilization are the environmental impact and the durability of WSA.

2.2. Variability of WPA

WPA is a byproduct of many materials and wastes from paper manufacturing. During incineration, depending on the materials used, WPA physical and chemical properties of WPA may change. On the other hand, to reduce exhaust gases and better regulation during incineration, the selection of materials becomes important. This also provides other benefits for the WPA, resulting in a better homogenous material with less diverse physical and chemical properties. To evaluate the variability of WPAs, samples were taken from the paper recycling plant. The experiments for the variability were including loss on ignition (LOI), X-ray Fluorescence (XRF), powder diffraction technique (XRD) for mineralogical characterization, and particle size distribution. The frequency of each experiment is shown in Table 1.

Table 1. Test frequency of experiments

Test	**Frequency test**	
	Monthly	Quarterly
LoI	X	
XRF	X	
XRD		X
Particle size distribution		X

A total of 12 samples for WPFA and 12 for WPBA were collected from 2018 to 2019. The LoI was carried out in accordance with EN 1744-1. Figure 1 demonstrates the LoI variability for WPFA and WPBA. The average loss of ignition for WPFAs is 17.4% with a variation of 6.4% (as shown in Figure 1 with a horizontal gray bar), while WPBA obtained a value of 12.5% and a variation of 29.7%. These results show the high variability of WPBA in relation to WPFA.

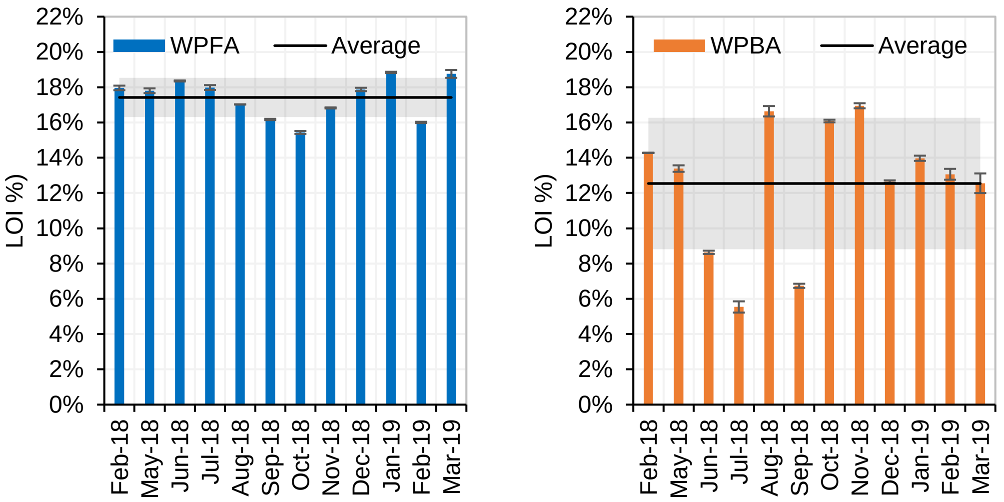

Figure 1. LOI for variability ash samples.

The FRX is carried out for ashes from February 2018 to April 2019. The results for WPFA and WPBA are shown in Table 2 and Table 3. Figure 2 and Figure 3 show the variation of the main four elements on both waste paper fly ash and bottom ash, respectively.

Table 2. Chemical composition of waste paper fly ashes.

Compound (wt,%)	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**TiO_2**	**SO_3**	**Fe_2O_3**	**P_2O_5**	**Cl**	**Other**
Feb-18	48	12	11	1.7	1.0	0.7	0.7	0.8	3.3	1.3
May-18	48	12	12	1.7	1.0	0.7	0.8	1.0	1.5	1.8
Jun-18	49	11	11	1.6	0.9	0.5	0.8	0.0	1.7	2.2
Jul-18	49	11	13	1.5	0.9	0.6	0.8	0.6	1.8	1.3
Aug-18	47	12	11	1.6	1.4	1.0	0.9	0.8	2.7	2.4
Sep-18	49	13	10	1.7	1.2	1.1	1.0	0.8	2.3	2.4
Oct-18	48	12	12	1.6	1.3	1.0	1.0	0.9	2.2	2.5
Nov-18	48	12	12	1.5	1.2	0.9	0.9	0.8	2.6	2.2
Dec-18	49	12	9	1.6	1.3	1.0	0.9	0.7	2.5	2.2
Jan-19	48	10	11	1.4	1.2	0.9	0.9	0.5	3.0	2.2
Feb-19	48	12	11	1.7	1.4	1.1	1.0	0.9	2.5	2.5
Mar-19	50	10	11	1.4	1.1	0.8	0.8	0.5	2.5	1.9

Table 3. Chemical composition of waste paper bottom ashes.

Compound (wt,%)	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**TiO_2**	**SO_3**	**Fe_2O_3**	**P_2O_5**	**Cl**	**Other**
Feb-18	39	28	10	1.3	0.9	0.7	1.1	0.8	1.2	1.0
May-18	44	22	10	1.5	1.4	1.1	1.1	1.0	0.8	1.6
Jun-18	52	18	11	1.6	1.3	0.9	1.2	1.0	1.1	1.4
Jul-18	45	31	7	1.4	2.0	2.0	1.1	1.2	0.7	1.8
Aug-18	44	19	9	1.4	1.4	1.1	1.1	0.7	1.3	2.5
Sep-18	48	26	7	1.4	1.8	2.2	1.2	1.0	1.0	2.9
Oct-18	48	13	12	1.7	1.0	0.8	1.2	0.7	1.4	2.0
Nov-18	47	14	10	1.5	1.1	0.8	1.0	0.6	3.0	2.1
Dec-18	47	19	9	1.5	1.5	1.5	1.4	0.7	1.3	2.6
Jan-19	45	18	10	1.5	1.4	1.2	1.2	0.7	1.5	2.9
Feb-19	46	18	10	1.5	1.5	1.4	1.3	0.8	1.4	3.0
Mar-19	48	18	9	1.5	1.3	1.3	1.1	0.7	1.3	3.0

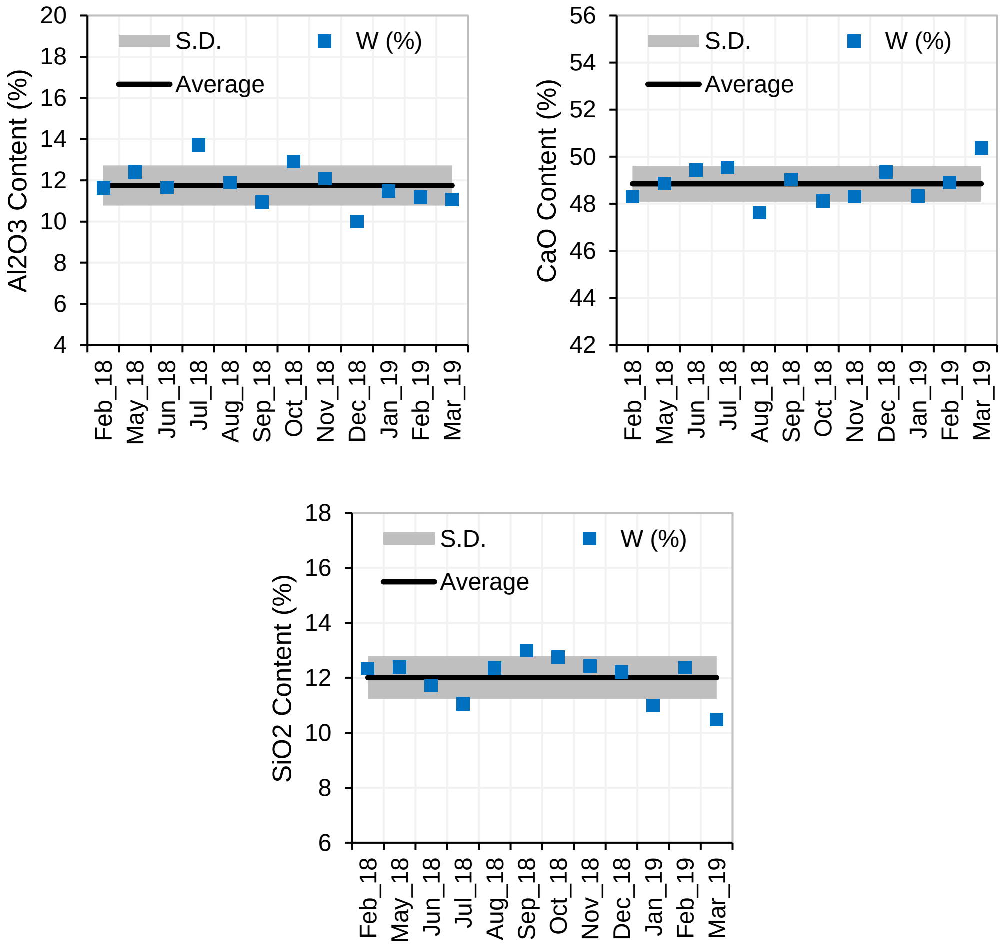

Figure 2. WPFA element content variation for CaO, SiO_2 and Al_2O_3.

The variation in WPFAs for three main elements CaO, SiO_2, and Al_2O_3 were 1.6%, 6.5%, and 8.3%, respectively. For WPBA, the CaO, silicon dioxide, and aluminum oxide variation were 7.2%, 26.2%, and 14.6%, respectively. More diversity was observed for WPBA samples.

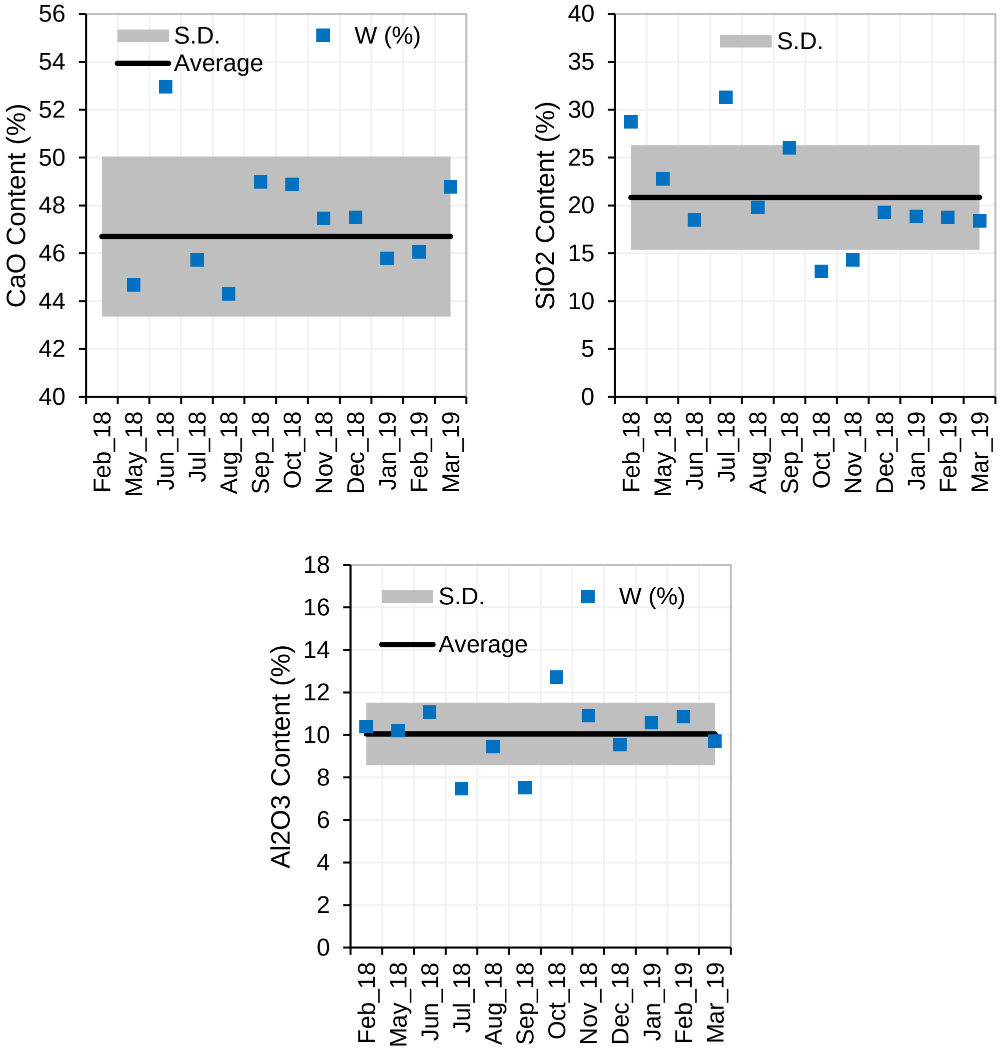

Figure 3. WPBA element content variation for CaO, SiO_2 and Al_2O_3.

Figure 4 represents the X-ray diffraction analysis for WPFA and WPBA, respectively. In both, WPFA and WPBA, there are some minor differences, however, the traces of main crystalline phases like lime, portlandite, and quartz can be seen.

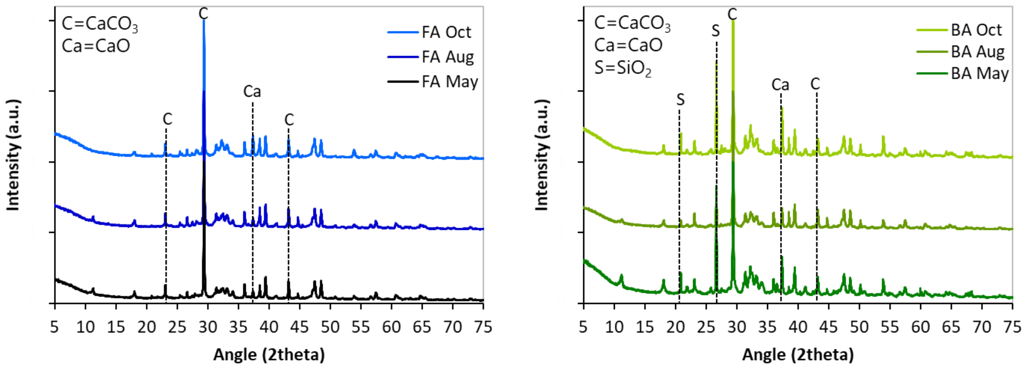

Figure 4. variability in XRD samples for WPFA and WPBA.

Particle size distribution is carried out using laser diffraction method as shown in Figure 5. WPFA obtained very similar size distribution, whereas WPBA obtained some minor size distribution.

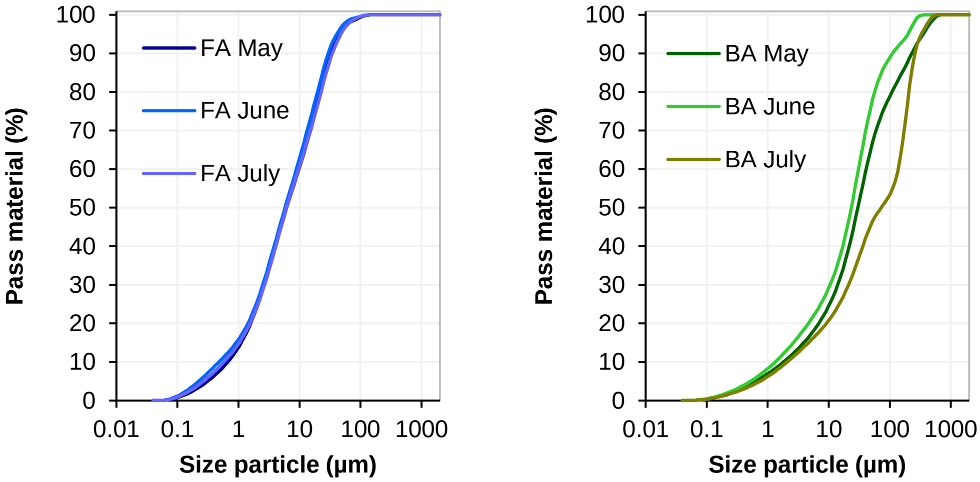

Figure 5. variability in particle size for WPFA and WPBA.

The one-year sampling from the paper plant gives good information about the variation of the ashes and determines whether they are viable to use as cementitious materials.

2.3. Environmental aspects of WPA

Moving towards a sustainable society requires developing more sustainable new materials and methods while lowering waste production. Since most new materials come from waste or are any by-product of other materials, their environmental impacts are unknown and should be deeply studied.

The main sectors that primarily are producing organic hazardous waste are agro, food and paper and pulp industries [19]. Owing to their organic nature, these wastes are used to dumped into the environment. Prior to the 1970s, pulp and paper effluent was frequently dumped untreated into rivers, which affected the ecosystem due to having a high amount of organic loads, solid content, and toxic compounds.

Most frequently, recycling waste paper involves dissolving used or old paper in a solution of water and chemicals. This process, alongside the cutting and heating, leads to a breakdown of cellulose strands; the resulting combination is known as pulp. It is then cleaned, de-inked, bleached, and combined with water after being passed through screens to remove any plastics (particularly from plastic-coated paper) that may still be present in the mixture. After that, new recycled paper can be manufactured from it. The process of recycling and producing pulp and paper generates different types of waste such as dregs, grits, lime mud, and pulp mill sludge.

Some of these wastes can be used as fuel. The end result of using these wastes as fuel is waste paper ash (WPA). However, during recycling paper some chemical material is used which may have an impact on environmental aspect of WPA.

In accordance with European regulations [20], waste can be recovered if its leachable elements are below a certain threshold. The council of the European union for waste that ends up at landfills defines some criteria. The first step is to do a basic characterization of the waste and define its type, origin, and composition, and then, if necessary, in the next step to do a compliance test to verify the finding in the first step. Moreover, according to the council, wastes at landfills can be categorized as inter waste, non-hazardous wastes, and hazardous wastes. Inert waste can be categorized as glasses, concretes, bricks, etc Table 4**Error! Reference source not found.** shows the list of wastes acceptable at landfills for inert waste without testing.

Table 4. Acceptable wastes at landfills without testing (adapted from [20]).

EWC code	**Description**
101103	Waste glass-based fibrous materials
150107	Glass packagingGlas
170101	Concrete
170102	Bricks
170103	Tiles and ceramics
170107	Mixtures of concrete, bricks, tiles and ceramics
170202, 191205 and 200102 (only glass)	Glass
170504, 200202	Soil and stones

However, if the waste is not on this table, it is necessary to carry out the leaching tests for different leachable components and compare the results with Table 5.

Table 5. Leaching limit values for granular waste acceptable at landfills.

Component	Inert waste	Non-hazardous waste	Hazardous wastes
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	1.7
Cr total	0.5	10	15
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
Chloride	800	15000	25000
Fluoride	10	150	500
Sulphate	1000	20000	50000

Note: L/S=10 l/kg. Units: mg/kg

Some studies using other types of paper waste indicated that waste coming from paper manufacturing is safe. The results obtained from primary sludge revealed no harmful element was leached to damage the environment [21]. Moreover, paper mill sludge was categorized as inert waste, although under very rare conditions (not by nature, only in laboratory test) can be harmful [22]. Nevertheless, there is a need to study environmental impact of WPA since it undergoes different process and rapid combustion and cooling which results in more amorphous phases. These amorphous phases are usually metastable under environmental conditions [23]. Additionally, the pre-treated material used for combustion can be varied, and may contains some dangerous elements such as lead, barium or cadmium [24]. For these reasons, the environmental impact of WPA becomes very important and should be studied.

2.4. Environmental monitoring of WPFA (case study)

An experimental field trial was performed in Villamayor de Gállego (Zaragoza, Spain). The goal was to stabilize 25 cm in depth of a 1 km long road with only WPFA. The environmental monitoring consisted of taking samples from different parts of the area to determine the WPFA effect on the environment. The samples were taken from the natural soil, before and after stabilizing, from ground and surface water, and from vegetation.

The study of the trace element content in natural soil and dust gathered from the vegetation showed no distinguishable variations before and after construction. However, for the stabilized soil, some elements such as Antimony and Vanadium increased by around 15 %, Aluminium, Cobalt, Copper by 10 %, and Manganese, Barium, and Zinc raised 5%. The rest of the elements stayed constant for stabilized soil.

Furthermore, to evaluate the mobility of heavy metals beneath the stabilized soil, 3 piezometers at the depth of 2 m and 3 m bore holes at depth of 10 m were placed.

Table 6 shows the results obtained leaching concentration from the field trial in Zaragoza, Spain. Comparing these results with inert waste values, only Antimony is considered high, but still less than non-hazardous waste value. Moreover, the data collected from piezometers showed no metal mobility, and all the elements stayed below the inert waste threshold.

Table 6. Field trial stabilized soil leaching values.

Component	**Inert waste**	**Non-hazardous waste**	**Stabilized soil with WPFA**	**Leached piezometer**
As	0.5	2	0.01	0.0009
Ba	20	100	1.4	0.05
Cd	0.04	1	0.01	0.001
Cr total	0.5	10	0.31	0.005
Cu	2	50	0.37	0.16
Hg	0.01	0.2	0.01	0.0005
Mo	0.5	10	0.2	0.02
Ni	0.4	10	0.2	0.005
Pb	0.5	10	0.2	0.018
Sb	0.06	0.7	0.19	0.009
Se	0.1	0.5	0.05	---
Zn	4	50	0.2	0.10
Chloride	800	15000	761	272
Fluoride	10	150	< 5	0.17
Sulphate	1000	20000	< 50	629

Note: L/S=10 l/kg. Units: mg/kg

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Chapter 3

3.1. Waste paper ash as a hydraulic road binder: hydration, mechanical and leaching considerations

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Waste paper fly ash (WPFA) and bottom ash (WPBA), derived from fluidized bed combustion of a paper recycling plant, exhibit cementitious properties owing to its mineralogical composition, and hence, could be proposed as a hydraulic binder. However, it may also contain some traces of heavy metals. Considering it is necessary to understand the effect of reusing any kind of waste on the environment, this study proposes of reusing WPFA/WPBA as a hydraulic road binder by evaluating its mineralogical composition and leaching activity. Chemical, physical, and mineralogical properties of raw WPFA/WPBA and the microstructural evolution of binders were carried out. Results showed that both ashes undergo hydration reactions while showing some cementitious properties by forming C-S-H gel, Friedel's salt, and calcite. According to the European standard EN 13282-1, both WPFA and WPBA can be categorised as N1 considering they reach 5.3 and 3.6 MPa, respectively, at 56 days. Furthermore, the mechanical performance of various soils was improved by using WPFA and WPBA as a binder. From the environmental point of view, the amount of barium in WPFA and WPBA, which is the main problem, was significantly decreased by using these ashes as a binder.

Keywords: waste paper ash, WPA hydration, soil stabilisation, leaching, heavy metals.

3.2. Introduction

The pulp and paper industries produce high amounts of waste. Considering Europe is a major pulp and paper producer, generating over 90 million tonnes of paper and board in 2019 alone (CEPI, 2019), this sector has been criticised extensively owing to the rising concerns of global environmental issues (Kinuthia, 2016).

Paper manufacturing processes generate various types of waste, such as dregs, grits, lime mud, and pulp mill sludge (Monte et al., 2009), which have been sent to landfills over the past decades. However, nowadays, there is a new trend in the paper and pulp industry that focuses on sustainability. Therefore, developed countries like Spain, Germany, and The Netherlands are reducing landfilling by banning certain types of waste streams from going into landfills (Monte et al., 2009).

Similarly, paper industries are trying to reduce their footprint in the environment by recycling. In Europe, the recycling rate in the pulp and paper industry was approximately 72% in 2019, which increased by 0.4% compared to the previous year (EPRC, 2019). However, the chemical used to remove ink from used papers can be harmful to the environment. Additionally, printing inks contain heavy metals (Bajpai, 2014).

Among all the wastes produced by the pulp and paper industry, pulp mill sludge and pulp rejects can be potentially used as alternative fuels in waste to energy plants (WTE) to produce electricity or steam (Simão et al., 2018). WTE uses different combustion technologies, one of which is the fluidised bed combustion (FBC) technology that allows greater flexibility when using fuel and improved heat transfer during combustion. FBC is made up of fuel in pieces (in pulp and paper factories, it includes rejects from the pulper, sands, sewage sludge from paper recycling, and plastics that have been pre-treated) and the bed itself (ash, clay, and additional materials). Considering combustion of the bed is regulated, the temperature is limited to 850-900 ºC. The bed supports solid fuel only, while air is pumped upwards during combustion to provide oxygen. Therefore, swirls that favour the mixture of gas and fuel is formed. If the direction of the gas changes, the ashes fall owing to gravity. The physical and chemical properties of the ash can differ depending on where it is collected. In the first part of process, bottom ashes and slags are collected before the smoke treatment and identified as waste paper bottom ash (WPBA).

The pollutant exhaust gases enter a filter chamber during combustion to eliminate HCL, HF, and heavy metals. To remove other pollutants such as SO_2 and organic gases, the gases should come in contact with the lime solution.

Owing to the type of fuel incinerated in the boiler, the exhaust gases are highly contaminated with high concentrations of hydrochloric acid (HCL). Hydrated lime ($Ca(OH)_2$), along with HF and SO_2, is used to absorb these acid gases. The system automatically controls the dosage of hydrated lime to be below 10 mg/Nm^3 depending on the HCl concentration in the exhaust gases in the chimney. In addition, activated carbon is used to absorb heavy metals gaseous, dioxins, and furans. Hydrated lime and activated carbon are injected by the common collector located before the entrance for the gases into the bag filters, where they react with the polluting products of the gases and are retained in the bag filters. Each filter comprises cleaning nozzles in the upper part, which blow counter-flow in pulses during the removal of ash, lime, and carbon, and a bottom ash cleaning system, which comprises a double scraper that rotates around a central axis and drives the ashes fallen from the filters to an auger. Then, the auger discharges the ash onto a pneumatic conveyor, which sends it to the fly ash silo. Therefore, waste paper fly ash (WPFA) is considered to be a mixture of hydrated lime, activated carbon, and ash collected after the smoke treatment.

Compared to WPFA, WPBA is coarser and has a darker colour owing to high amounts of Fe_2O_3 (Aïtcin, 2016). Its particle sized distribution is reported with d_{50} particles of ~90-100 mm (Mavroulidou, 2018; Spathi et al., 2015). Table 1 shows the chemical composition of waste paper ash (also known as Waste Sludge Ash (WSA), Paper Sludge Ash (PSA), and Waste Paper Sludge Ash (WPSA)). Paper sludge can be divided into the following categories: waste coming from wood virgins (primary sludge), waste paper sludge generated by removing the ink from post-consumer fibre, called de-inking paper sludge, activated sludge from the secondary system, called secondary sludge, and waste paper and active sludge combined called combined sludge (Boni et al., 2004). The pH of WPA is reported to be higher than 12 (Mozaffari et al., 2009; Spathi et al., 2015). Likewise, it was found that WSA contained a small amount of metallic aluminium (Segui et al., 2013), which could expand in an alkaline environment. Similarly, several studies have reported the reaction between water and free lime, which leads to the expansive reaction of the formation of portlandite (Bai et al., 2003; Mozaffari et al., 2009).

Table 1: Range of values in the literature of chemical composition for WPA (Bai et al., 2003; Bui et al., 2019; Chen et al., 2019; Ferrándiz-Mas et al., 2014; Kinuthia et al., 2001; Mozaffari et al., 2009; Sadique et al., 2019; and Segui et al., 2013).

Element	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI
Composition [%]	42-57	17-28	3-19	0.3-5	3-5	0.3-14	1.2-6

The main minerals of WPA are quartz, lime, calcite, and calcium silicate (Kinuthia et al., 2001; Segui et al., 2013; Spathi et al., 2015). However, beside these minerals, Kinuthia (Kinuthia et al., 2001) found Anorthite and Gehlenite, which indicated that WSA may have significantly high amorphous silica and alumina content.

Bai (Bai et al., 2003) found that one day after WPA hydration, the CaO peaks disappear owing to fast hydration while $Ca(OH)_2$ remains constant. Furthermore, the WPA hydration at 90 days and the presence of vaterite was determined (Bai et al., 2003). Derivative thermogravimetric (DTG) studies showed traces of C-S-H gel in WSA, which increased after 90 days (Bai et al., 2003). Furthermore, the existence of ettringite was proposed owing to the presence of SO_3 in the chemical composition of WSA. At approximately 230 °C, the dehydration of both C_4AH_{13} and $C_3A.0.5CC0.5CH.H_{11.5}$ at 1 day gradually increases up to 90 days (Bai et al., 2003).

Owing to these problems, researchers have tried to determine a way to use this waste in different fields. Civil engineering is considered a promising field, considering WPA can be used as supplementary cementing material (Frías et al., 2008; Sadique et al., 2019) in mortars and concrete (Bai et al., 2003; Kinuthia et al., 2001; Kinuthia and Gailius, 2001; Mozaffari et al., 2009), and for soil stabilisation (Khalid et al., 2015, 2012; Mavroulidou, 2018; Segui et al., 2013).

Segui (Segui et al., 2013) studied the usability of WPA as a binder in soil stabilisation by treating the soil with WPA, a mixture of gypsum and WPA, and two commercial binders (Ground Granulated Blast Furnace Slag (GGBFS) and steel slag; GGBFS and clinker). The treated soil with WPA obtained strengths of 0.5 MPa at 3 days and 5.7 MPa after one year. Additionally, WPA can be optimised by adding a mixture of 80 wt% WPA and 20 wt% gypsum, which improves the compressive strength from 0.5 MPa to 1.3 MPa at 3 days and up to 7 MPa in a year. The result showed that WPA can improve the strength of treated soil, similar to commercial binders.

Khalid (Khalid et al., 2012) studied the use of different concentrations (2% to 14%) of WPSA for treating clay soil and curing for 0, 14, and 28 days. The result showed that adding 10% WPSA provided the highest compressive strength and curing at 14 days further improved the compressive strength by 25%. By curing at 28 days, the compressive strength improved by 15%. However, the study does not mention the reason for the decrease in compressive strength on adding higher concentrations of WPSA. This could be attributed to the fact that WPSA contains high amounts of expansive material (free lime). Additionally, WPSA is a porous material, and hence, higher concentrations of WPSA could decrease its effectiveness (Spathi et al., 2015).

Khalid (Khalid et al., 2015) continued the previous mentioned study by conducting scanning electron microscope (SEM) experiments on treated soil with WPSA. Results showed the presence of C-S-H gel, calcium aluminate hydrate, and ettringite.

Mavroulidou (Mavroulidou, 2018) stabilised three different types of clay soils with five different types of binders, including two types of cement and lime, and one type of WPA. In most cases, the soil treated with WPA showed its effectiveness in unconfined compressive strength, plasticity characteristics, water retention, and volumetric stability. Furthermore, this study showed that using WPA could be beneficial for environmental and economic concerns with zero cost (except transportation). Additionally, compared to lime, soil treated using WPA requires less water.

One of the main aspects of using waste material is its effect on the environment. According to European regulation, waste can be recovered if the number of elements that can leach into underground water is below a certain threshold (Kuokkanen et al., 2008). A study conducted leaching tests to evaluate the effect of primary sludge (coming from virgin wood fibre) on the environment. The result showed that the release of heavy metals from primary sludge did not harm the environment (Boni et al., 2004). Another leaching study (Kuokkanen et al., 2008) showed that paper mill sludge showed could be problematic owing to the release of certain elements under certain conditions (leachable with the mixture of HF + HNO_3 + HCl); however, it is not likely for this to occur in the nature. Therefore, paper mill sludge was categorised as the inert phase. Furthermore, other types of products or waste produced during paper and pulp manufacturing, such as de-inking or secondary sludge, are yet to be evaluated. For example, WPA undergoes rapid combustion and cooling, resulting in more amorphous phases. These amorphous phases are usually metastable under environmental conditions (Assi et al., 2020). Furthermore, during combustion, the pre-treated material can be varied, which causes a change in the physical and chemical properties of WPA. Moreover, the pre-treated materials in bed combustion could release some heavy metals like lead, cadmium, and barium from the de-inking process, which could contaminate the soil and groundwater (Bajpai, 2014). Lastly, considering heavy metals are assumed to be a result of the ink and de-inking process (Bajpai, 2014), the type and amount of pollutants in the ashes depends on the raw material used, the pre-treatment process, and the type of waste combustion from recycled paper production.

This study assesses the use of WPFA and WPBA generated from paper recycling plants (using paper as its raw material) as a binder for soil stabilisation. For this purpose, the physical, chemical, and mineralogical characteristics of WPFA and WPBA were determined and then the characterization was completed by studying the reactivity of these ashes. The compressive strengths of WPFA and WPBA mortars were studied according to the European standard (UNE-EN 13282-2, 2016). Furthermore, leaching tests were carried out to analyse the effect of these ashes on the environment. Herein, some successful soil stabilization using these ashes are explained.

3.3. Materials and methods

3.3.1. Materials

3.3.1.1. Waste Paper Ash (WPA)

The WPFA and WPBA studied in this study were supplied by SAICA (Sociedad Anonima Industrias Celulosa Aragonesa), a Spanish pulp and paper manufacturer that uses only recycled paper as a raw material. Saica operates an energy valorisation plant that burns rejected waste streams produced in four paper mills to generate 49 MWhe.

The chemical composition of both ashes was determined by the X-ray Fluorescence method, with a Spectrometer of Philips/PANalytical, model PW2400. The main elements in both ashes are calcium, silicon, and aluminium, with small amounts of magnesium and chlorine, as summarised in Table 2.

Table 2: Chemical composition of the raw materials (WPFA and WPBA)

Chemical composition	**Mass fraction (%)**	
	WPFA	**WPBA**
CaO	48.90	47.38
SiO_2	11.98	20.11
Al_2O_3	11.76	10.01
MgO	1.61	1.55
Fe_2O_3	0.93	1.22
ClO	2.35	1.38
TiO_2	1.21	1.46
SO_3	0.92	1.35
P_2O_5	0.73	0.87
Na_2O	0.83	0.92
Other	1.16	1.29
LOI (%)	17.3	11.8
Free lime content (%)	6.36	6.44
Density (g/cm^3)	2.68	2.72
pH	12.3	11.9
Conductivity (mS/cm)	11.14	7.90

Figure 1 shows the particle size distribution of WPFA and WPBA. The as-received WPFA and WPBA show d50 particles of ~6.4 µm and 37 µm, respectively. Therefore, WPBA exhibited a coarser particle size than WPFA.

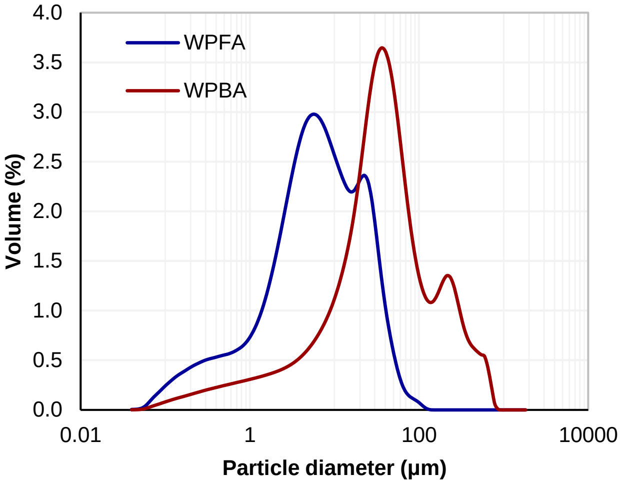

Figure 1: Particle size distribution of WPFA and WPBA

Scanning electronic microscopy (SEM) studies were conducted in a FEI SEM equipped with energy dispersive X-rays microscopy model ESEM Quanta 200, XTE 325/D8395. Figure 2 shows a general view of SEM. Both ashes exhibited very irregular shapes and were porous.

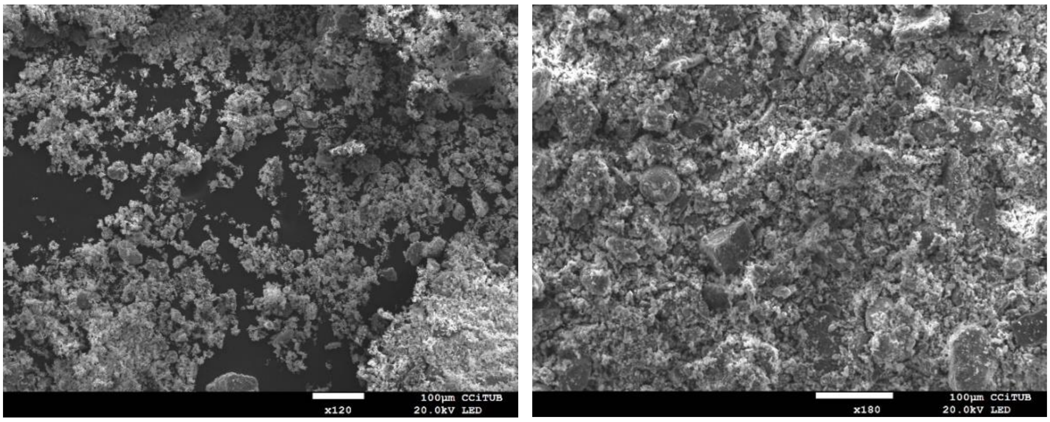

Figure 2: SEM overall view of WPFA (left) and WPBA (right).

This study used the powder diffraction technique (XRD) to identify the crystalline phases (comprising calcium, aluminium, and silicon) in WPA using a Philips X-ray Diffractometer with a PANalytical X'Pert PRO MPD Alpha 1 diffractometer with Cu Kα radiation (λ = 1.5406 Å, 45 kV – 40 mA). The results were interpreted using EVA software (database PDF-2).

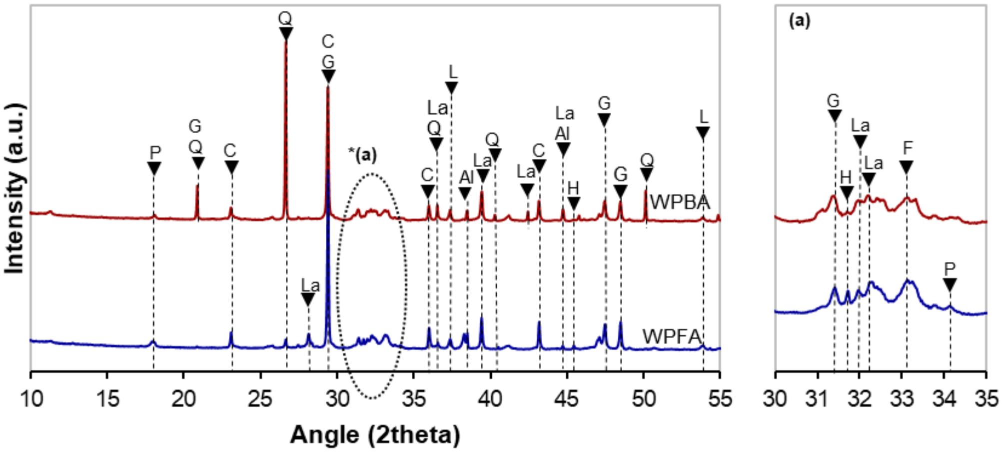

Figure 3: WPFA and WPBA diffractograms - C: Calcite ($CaCO_3$), P: Portlandite ($Ca(OH)_2$), Q: Quartz(SiO_2), L: Lime(CaO), La: Larnite(Ca_2SiO_4), G: Gehlenite ($Ca_2Al_2SiO_7$), H: Halite (NaCl), and A: Aluminium (Al).

Figure 3 shows the presence of calcite, lime, quartz, larnite, aluminium, and halite in both ashes. Additionally, small amounts of portlandite were found owing to the moisture in the environment. Some similarities were observed in both ashes compared to those used in other investigations, such as lime and calcite (Bai et al., 2003; Kinuthia et al., 2001; Segui et al., 2013; and Spathi et al., 2015). In WPBA, the peak of quartz is much bigger in WPBA (26.6 2θ) compared to that in WPFA, as shown in Figure 3 and Table 2. The higher concentration of quartz in WPBA was mainly due to the fluidised bed. Figure 3(a) shows a magnification from 30 to 35 2θ degrees to better identify the peaks. A small hump was observed in this region, associated with some amorphous phase. Additionally, the free lime (CaO) content was determined in accordance with EN 451-1, 2017, and obtained 6.36 and 6.44 wt.% for WPFA and WPBA, respectively. Furthermore, the density was determined using standard UNE 80103 (UNE 80103, 2013) and obtained 2.68 g/cm³ and 2.72 g/cm³ for WPFA and WPBA, respectively.

3.3.2. Hydration analysis of WPA

Isothermal conduction calorimetry was conducted using Calmetrix I-CAL 4000 calorimeter at 20 °C with 4 g of total binding material and water to study the hydration process of WPFA and WPBA. The room temperature was 20 °C and external hand-mixing of the paste samples was conducted for less than 1 min using a vortex mixer directly in the plastic vials. Then, the mixture was loaded into the equipment to measure the heat flow of the hydration process for the first 22 h.

XRD, Thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR) were used to identify and characterise the mineralogical evolution at 7, 28, and 56 curing days. For TGA, a Mettler Toledo model TGA / DSC 1 Thermal Analyser was used with 10 µg of material with temperature intervals between 30–1000 °C, a N2 flow of 50 ml/min, and a heating rate of 10 °C/min. Before each test, the samples were stabilised at 100 °C for 15 min. For FT-IR spectrometer Frontier (Perkin Elmer), each FTIR spectra were acquired with 16 scans with a spectral resolution of 4 cm-1 over a range of 4000-250 in attenuated total reflection (ATR) mode.

The hydration of the samples was stopped using the solvent exchange method (Snellings et al., 2018). The samples were then pulverised to a particle size below 63 μm, homogenised, and ready to use in the techniques mentioned above.

3.3.3. Mechanical behaviour of WPA mortars

The compressive strength test was conducted according to standard EN 196-1, 2016 for hydraulic road binder (UNE-EN 13282-2, 2016) using the prism moulds. Considering the standard (EN 196-1, 2016) suggests making a mortar with dimensions 16×4×4 cm with 1350 g sand and 450 g cement, which in this case is replaced with WPFA and WPBA, and 225 g water is needed. The ash is mixed with sand and water, as explained in (EN 196-1, 2016); however, instead of pouring it into the mould, it was set to rest for 30 min. During this time, evaporation was avoided.

Owing to the different properties and more water absorption of WPFA and WPBA compared to cement, a paste was made according to the quantity mentioned in the standard; however, it was too dry to compact with jolting apparatus. Therefore, a manual rammer was used for compaction, as shown in Figure 4.

After 30 min, the material was poured into the mould and compacted with the rammer using normal Proctor energy by adding approximately 260 g per layer, and further compacted in 2 layers with one additional layer to smooth the surface (third layer).

Figure 4: Compaction rammer.

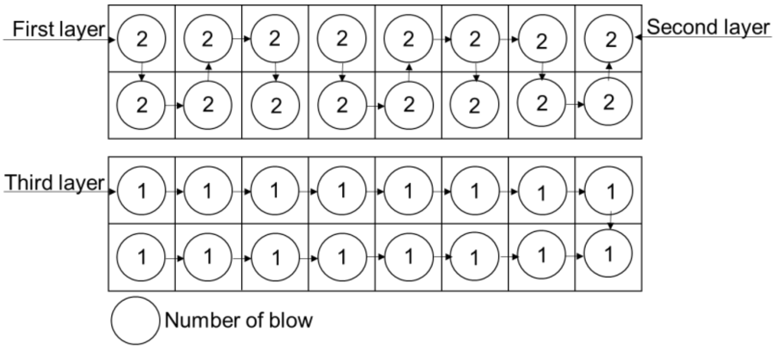

Figure 5: Mortar compaction method (number in the circle is the number of the bows).

Figure 5 shows the procedure of mortar compaction with a 500 g rammer, which was conducted for each batch of three specimens. The height of the fall was 200 mm with two blows for each section. However, only one blow was considered for the third layer to make the surface smooth. The specimens were cured at 20 ℃ and 95% ambient relative humidity and were tested in flexion and compression at 7, 28, and 56 days. Three specimens were tested for each curing period. The demoulding of the samples took place after 5 d instead of the following day, considering the samples did not gain enough strength for demoulding, which could damage the sample.

3.3.4. Environmental impact (leaching test)

One of the problems of using new wastes in construction is its environmental impact. Therefore, leaching tests, which are widely used to estimate the release potential of constituents from waste materials generated from possible waste management activities, such as recycling or reusing, were conducted on WPFA and WPBA to evaluate their effect on the environment according to EN 12457-2, 2002. For these tests, a liquid to a ratio of 10 l/kg was used. Considering the material particle size was less than 4 mm, no grinding was used in the test. pH and conductivity, the amounts of heavy metals. Results were compared to the limit values for the acceptance of waste at inert waste landfills according to European Council Decision 2003/33/EC (CEC, 2002).

3.4. Results and discussion

3.4.1. Initial hydration of WPA: Isothermal calorimetry

The isothermal results are shown in Figure 6. As soon as WPA becomes in contact with water, hydration takes place. The first liberation of heat, which corresponds to the dissolution of different ionic species, as shown in Figure 6(b) and (d). The initial heat increases in WPFA by increasing water from 15% to 30%. However, by 45% stays nearly the same, and by 60% decreases. It seems that 60% water is high enough to withhold the generated heat. At the same time, the dissolution of free lime, makes the solution alkaline, providing a suitable environment for releasing hydraulic components like silicates and calcium aluminates. This can be seen by the existence of hump in Figure 6.a and d (15% water from 5 to 22 hours) in both ashes. For the rest of the water ratios, this hump has been decreased. Eventually, this hump is vanished with 60% water due to the higher initial heat output. This hump only can be seen in WPBA with 15% water. The dissolution of free lime forms hydrated lime which is an expansive reaction. This expansion in the mix leads to lower workability, and hence, adding the water to the mix and setting it rests for a while (slaking) can improve the workability of these ashes. Another point is that to hydrate all the lime in the mixture, a maximum of 30% water is necessary for both ashes.

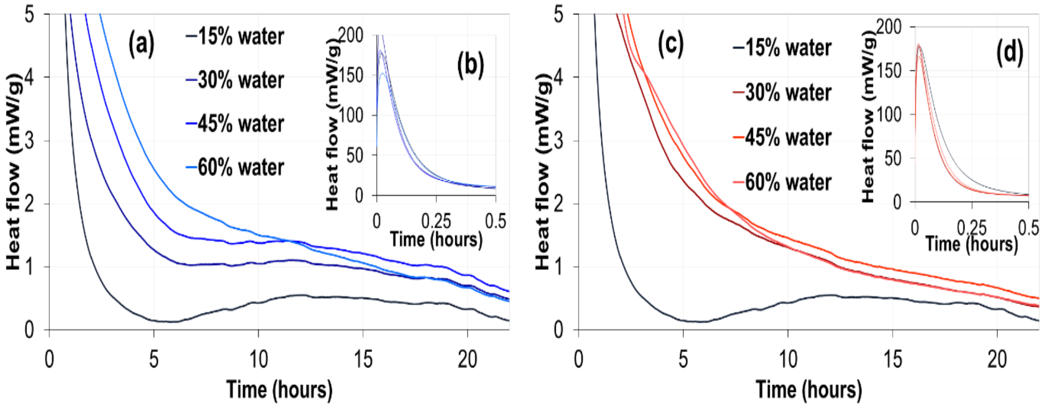

Figure 6: Isothermal calorimetry with WPFA and WPBA for 15, 30, 45, and 60% water.

3.4.2. WPA hydration analysis

Figures 7 and 8 show the changes in the mineralogical composition for WPFA and WPBA, respectively, at 7, 28, and 56 days. During hydration, a rapid consumption occurs in the peaks of principal CaO, which disappear after approximately 7 d. The dissolution of lime in the system makes the solution alkaline, resulting in the dissolution of other hydraulic components, which are approximately around the peaks at 30 to 35 2θ degrees (Figure 7(a) and Figure 8(a)) for WPFA and WPBA. All of the larnite and aluminium were consumed in 56 days.

Interestingly, while the lime is consumed, portlandite peaks disappear, indicating a rapid consumption of lime and portlandite simultaneously. While lime is being consumed and converted into portlandite, the portlandite is converted to calcite. This is indicated by the appearance of calcite in the XRD patterns, which gradually increase around peaks 23, 29, 36, and 39 2θ degrees and reach the maximum peak at 56 days.

Another phenomenon is the formation of Friedel's salt, and its reflection can be observed at 11.4° 2θ (Qian et al., 2006). This indicates that WPA is releasing some amount of chloride into the system, which can be seen in chemical composition

(Table 2). However, there is no evidence of any change in the intensities of the diffraction peaks of quartz and gehlenite, thereby indicating that these are not reactive phases.

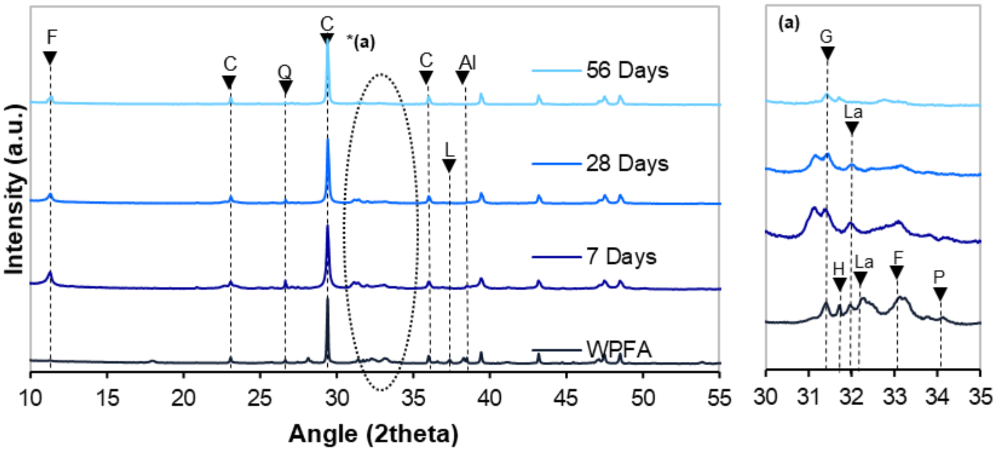

Figure 7: WPFA diffractograms for anhydrate after hydrating for 7, 28, and 56 days.

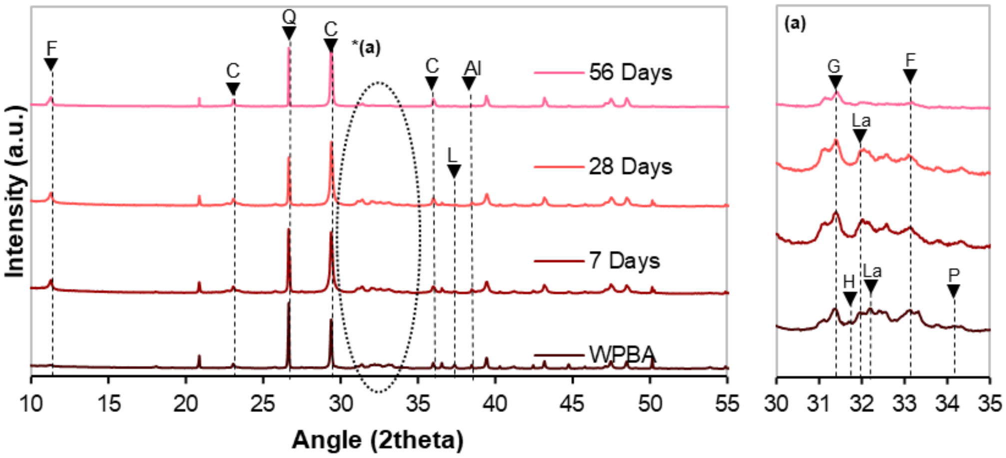

Figure 8: WPBA diffractograms for anhydrate after hydration for 7, 28, and 56 days.

Figure 9 shows the TGA results of WPFA and WPBA at 7, 28, and 56 curing days. Both ashes showed a peak around 142 to 152 ºC owing to the formation of C-S-H gel (Ashraf et al., 2009; Esteves, 2011; Trifunovic et al., 2010) and Friedel's salt. These peaks increase with ageing. The intensity of C-S-H gel in WPBA is smaller than that in WPFA.

The second peak, related to Friedel's salt, was identified by other authors at approximately 180~450 ºC (Birnin-Yauri and Glasser, 1998; Shi et al., 2017). As shown in Figure 9, it increases to approximately 3.6 %wt and 3.45 %wt in WPFA and 3 WPBA, respectively, from anhydrate to 56 days.

The Portlandite peak, which was identified by other authors at approximately 450~550 ºC (Dweck et al., 2000; Kinuthia et al., 2001; Sadique et al., 2019), disappeared in WPFA and WPBA. This peak showed a higher temperature of approximately 550~600 ºC for WPBA. The peak related to calcite identified at 680 ºC and between 760~780 ºC increased slightly in WPFA and by 2% in WPBA by the end of 56 days, respectively.

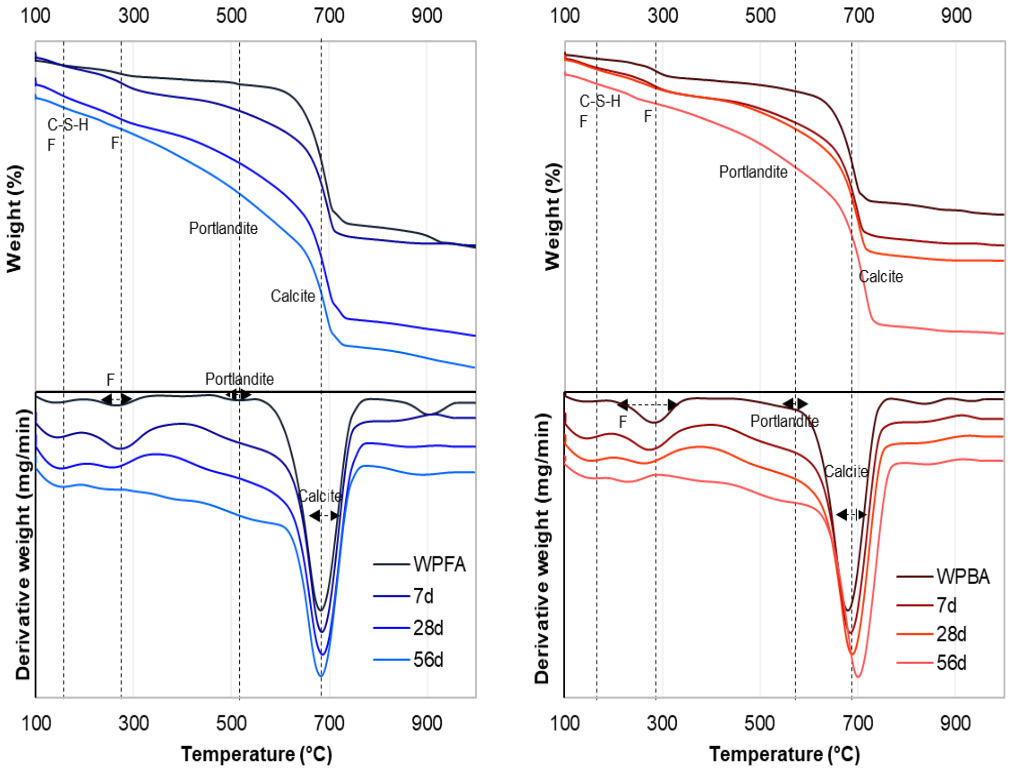

Figure 9: TGA traces for WPFA (a) and WPBA(b), where F: Friedel's salt.

The FTIR spectra of WPFA and WPBA at 7, 28, and 56 curing days are shown in Figure 10, which demonstrate the evolution of the characteristic compounds of the hydration process that was already characterised using the XRD and TGA techniques. Both ashes follow the same hydration reactions. Figure 10 shows the appearance of C-S-H gel as the hump increased around 3400-3500 cm^{-1} related to O-H peaks (Xu et al., 2022), and a second peak related to interlayer water for Friedel's salt, along with C-S-H gel around 1623 cm^{-1} (Qian et al., 2006). Other characteristic peaks of hydration and formation of C-S-H gel corresponded to a shift in the higher wavenumbers in the band between 800-1000 cm^{-1} and to a lower wavenumber in the band around 517 cm^{-1}, which in turn corresponded to the consumption of compound C2S (Tantawy, 2017). The Portlandite peak at 7 days disappeared completely whereas the calcite peaks around 1408 cm^{-1} increased. On comparing the two spectra of FTIR, WPFA showed slightly higher intensity in C-S-H, resulting in higher performance.

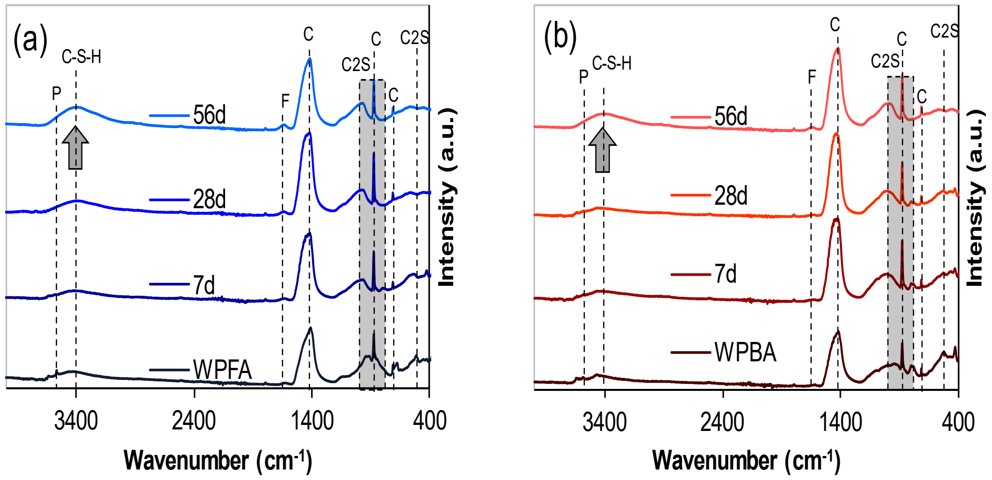

Figure 10: FTIR spectra of WPFA (left) and WPBA (right); where: P: Portlandite, F: Friedel's salt, and C: Calcite.

3.4.3. Compressive strength

The compressive strength results for both ashes for 7, 28, and 56 days are shown in Figure 11. The compressive strengths of the WPBA pastes were lower than those of the WPFA paste at all ages. At 7 days, WPFA and WPBA obtained compressive strengths of 4.8 MPa and 2.1 MPa, respectively. Both ashes showed particularly low strength development from 28 to 56 days. At 56 days, WPFA and WPBA reached 5.3 MPa and 3.6 MPa, respectively. WPFA showed a 68% improvement over WPBA at 56 days. This improvement can be seen in the microstructural studies (Figure 10), where the intensity of C-S-H gel was slightly higher in WPFA than WPBA, resulting in a higher strength owing to the better reactivity and smaller particle size of WPFA. The flexural strength of WPFA obtained a value of 1.1 MPa and increased by 64% to 1.7 MPa at 56 days. WPBA at 7 days obtained a flexural strength of 0.5 MPa, which increased by 30% to 1.4 MPa at 56 days.

It should be noted that the expansion was nearly eliminated considering the manual mortar compaction system and the delay time for these ashes. Furthermore, according to the European standard (UNE-EN 13282-2, 2016), these ashes were categorised as N1, thereby obtaining a compressive strength of over 2.5 MPa at 56 days.

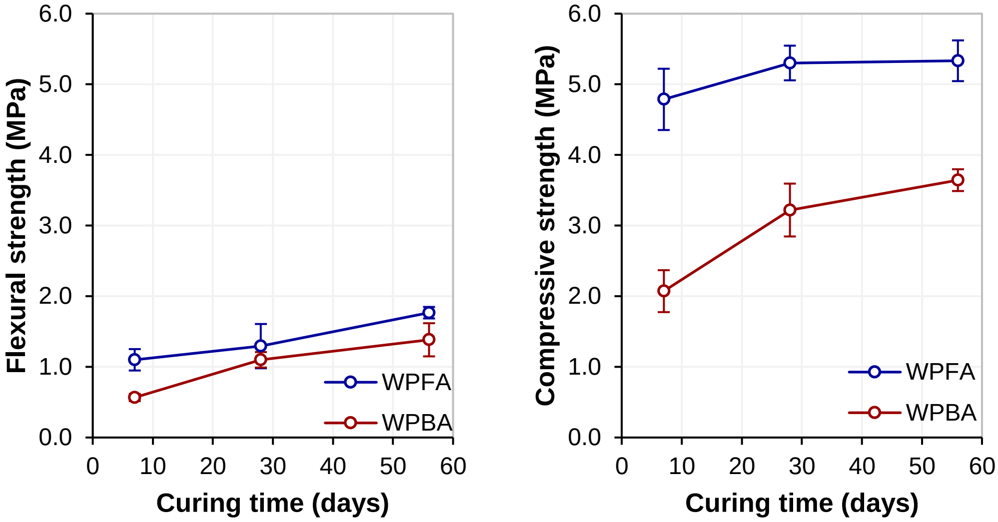

Figure 11: Mechanical properties of WPFA and WPBA.

3.4.4. Environmental aspect of WPA by means of leaching

Figure 12 shows the leaching results for WPFA and WPBA. Considering there is no exact value for the concentration of heavy metals when WPA is used as a binder, the obtained results were compared to the limit value mentioned in the European Council Decision 2003/33/EC (CEC, 2002). According to the European Waste Classification (EWC) (Environmental and forestry Statistics, 2010), WPFA is classified as EWC code 19 01 14, which corresponded to non-hazardous fly ash. WPBA is classified as EWC code 19 01 12 non-hazardous bottom ash and slag.

Figure 12 shows the released heavy metal in WPFA and WPBA. All elements in both WPFA and WPBA were lower than the limit values for inert wastes, except for barium. Some studies have suggested that high amounts of barium could harm the environment, such as the soil and plants. For instance, the study on barium toxicity on soybean plants found that it prevented photosynthetic activity (Suwa et al., 2008). However, other studies have shown that the uptake of barium is low owing to its low solubility (Cappuyns, 2018; Oskarsson, 2007). Another study (McBride et al., 2014) showed no correlation between the existence Ba in soil and vegetables, which could be due to the effect of soil pH, organic matter, and other soil properties on the metal solubility.

As mentioned earlier, Ba is considered water-insoluble; however, some of its compounds can be released and moved into groundwater in an acidic environment (acidic rains or acidic soil) (Oskarsson, 2007). However, owing to the hydration of lime, the solution becomes alkaline, and the presence of carbonate produces barium carbonate, which has low solubility in water (Gad, 2014).

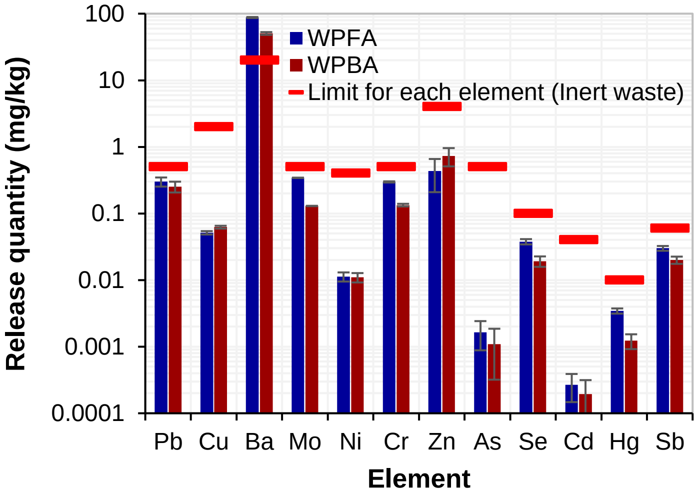

Figure 12: Heavy metals release for WPFA and WPBA.

3.4.5. Successful implementations of WPFA and WPBA as a hydraulic road binder

The assessment of utilisation of WPA as the main hydraulic component was determined by the means of mechanical properties in soil samples.

The WPA was collected between 2018 and 2020, and the compressive strength (CS) and CBR were determined on six different soils samples. Table 3 shows the detail of each stabilised soil, the particle size distribution of soils, amount of WPA in the soil, density, and the result for 7 d curing samples according to the European standards (UNE-EN-13286-41, 2003). The results showed that incorporating both WPFA and WPBA as the main binder can be successful in soil stabilisation. However, owing to the lower performance of WPBA, it can be used as a binder where a high mechanical requirement is not necessary.

To further investigate the leaching characteristics of WPFA in soil, samples #5 and soil #6 were prepared according to standard (UNE-EN-13286-41, 2003) and cured for 7 d at a temperature of 20 °C and 95% relative humidity. 3 wt% WPFA and 5.2 %wt WPFA were added in soil samples #5 and #6, respectively. Then, the samples were crushed and prepared for the leaching test according to EN 12457-2, 2002.

Table 3: Soil stabilisation using WPFA and WPBA as a binder.

Test	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
PSD (mm) Passed:						
40	100	100	100	100	100	100
16	90	84	87	79	100	86
12.5	80	82	80	68	100	76
4	65	75	55	37	99	44
2	42	72	43	29	98	32
0.5	37	55	30	21	98	19

0.16	31	34	17	12	83	12
0.063	30	28	10	8	73	10
Date collected	Jan/18	Jan/18	Feb/2018	Oct/18	Feb/19	Jan/20
WPA (%,wt)	5 % FA 7 % BA	5 % FA 7 % BA	5 % FA	5 % FA	3 % FA 4 % FA	5.2 % FA
Water (%,wt)	7 % 7.5 %	10 % 9.5	8.2 %	8 %	8 %	9 %
Proctor Density (g/cm^3)	2.1 FA 2.2 BA	1.95 FA 1.98 BA	1.98	1.98	1.94	2.14
CS using WPFA	0.65	0.86	1.87	2.77	n.m.	2.61
CS using WPBA	0.19	0.26	n.m.	n.m.	n.m.	n.m.
CBR using WPFA	102	117	n.m.	n.m.	26 47	n.m.
CBR using WPBA	46	55	n.m.	n.m.	n.m.	n.m.
Author	(Briceño, 2018)	(Briceño, 2018)	(Baloochi et al., 2020b)	(Baloochi et al., 2020a)		(Ruiz, 2020)

**FA: Waste paper fly ash, BA: waste paper bottom ash, CS: Compressive strength (MPa)*

The leaching results obtained from stabilised soil with WPFA showed that the amount of barium decreased significantly after incorporating WPFA. This may be due to two reasons. First, the barium in the stabilised soil does not eluate easily when it comes in contact with water (Glasser et al., 2008), and second, the ratio of WPFA to water, which previously was considered 10, decreased (because the amount of WPFA was 3 to 5%wt in the mix). Additionally, the amount of all metals, especially barium, decreased and reached the inert values suggested by the European Council Decision 2003/33/EC (CEC, 2002). Table 4 summarises the leaching results.

Table 4: Leaching results obtained from soil stabilisation.

Element	Soil 5+WPFA	Soil 6+WPFA	Limit (inert waste)	Limit (non-hazardous)
Pb	0.01 ± 0.001	0.1 ± 0.02	0.5	10
Cu	0.3 ± 0.1	0.1 ± 0.01	2	50
Ba	0.6 ± 0.1	1.4 ± 0.05	20	100
Mo	0.1 ± 0.01	0.09 ± 0.0007	0.5	10
Ni	0.01 ± 0.008	0.006 ± 0.0003	0.4	10
Cr	0.3 ± 0.06	0.3 ± 0.01	0.5	10
As	0.01 ± 0.002	n.d.	0.5	2
Se	0.02 ± 0.004	0.01 ± 0.0004	0.1	0.5
Cd	n.d.	n.d.	0.04	1
Hg	N/A	0.002 ± 0.0002	0.01	0.2
Sb	0.3 ± 0.0	0.6 ± 0.001	0.06	0.7
Zn	0.3 ± 0.1	0.3 ± 0.02	4	50

n.d.: Not detectable.

3.5. Conclusion

This study investigates the use of waste paper fly ash and bottom ash, produced from a paper recycling plant in Spain, as the main binder component in soil stabilisation. These ashes exhibited cementitious properties that form calcite, C-S-H gel, and Friedel's salt owing to the presence of chloride and small amounts of halite. Both WPFA and WPBA can be categorised as N1 according to the European standard by achieving compressive strengths of 5.3 MPa and 3.6 MPa, respectively. The higher strength and performance of WPFA are due to the finer particle size and more reactive phases.

From the environmental and utilisation perspective, the chemical properties of WPFA and WPBA can be altered depending on the material used during incineration, which can change the leaching properties of these ashes. The leaching test results showed that the level of barium should be considered when working with these ashes (69 mg/kg on average for both ashes). The amount of barium decreased significantly when WPA was used as a binder (< 1.4 mg/kg). On comparing the results with the main metalloids concentration established in the European directive (Directive 1999/31/EC), the final product (soil + WPFA) can be categorised as an inert material.

Finally, stabilisation of soil with WPFA and WPBA is possible and can be applied. The results of six different types of soil samples showed that WPFA could gain enough strength without incorporating any other type of binder. However, WPBA should be used in subbase soil or when a high-performance base is not needed.

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Chapter 4

4.1. Soil Stabilization Using Waste Paper Fly Ash: Precautions for Its Correct Use

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This paper deals with the valorization of waste paper fly ash (WPFA) as a binder for soil stabilization. The mineralogical characterization shows the presence of free lime, as well as some non-reactive and cementitious phases. The hydration of lime is an expansive reaction and can be problematic in soil stabilization. Therefore, to study its effect on stabilized soil, an in-house experimental set-up is proposed to measure the possible expansion. Furthermore, to study the effect of water reduction and delay time on strength, unconfined compressive strength with different mixes is conducted. The obtained results showed that using WPFA causes expansion in stabilized soil, but a delay time of 30 min, after mixing the material with water and then compacting it, can decrease the expansion. Additionally, decreasing the water content by a point of Proctor can be essential for improving the strength in soil samples, even reaching the same strength values as control samples cured at 7 days. Finally, all the results obtained in this study have shown that WPFA is a suitable material for use as a binder for soil stabilization while reducing its optimum water content, adding a proper delay time, and taking into consideration WPFA’s expansive behavior at the moment of its use.

Keywords: waste paper fly ash; soil stabilization; slaking of WPFA; compressive strength development; initial and final expansion of stabilized soil.

4.2. Introduction

A sector that has been criticized over the past decade is pulp and paper manufacturing [1]. This sector, other than being an intense consumer of resources, produces a large amount of waste [2]. Europe is the second largest pulp and paper producer in the world, holding 25% of world production. Producing pulp and paper generates 11 million tons of waste yearly [3,4]. It has been estimated that 25–40% of the municipal solid waste generated each year is related to paper [5].

To diminish the environmental impact of paper manufacturing, paper recycling had been growing, and some companies use only recycled paper as their raw material source. During paper manufacturing, waste sludge is produced that has been shown to be a valuable source of energy if being used in waste-to-energy plants. The resultant ash, which is called waste paper sludge ash (PSA or WSA) or waste paper ash (WPA), has been ending up in landfill sites. However, nowadays, Europe is facing the challenge of waste management, particularly industrial waste, due to some traditional disposals like landfills being restricted or banned.

In recent years, researchers have conducted many studies to find a solution for environmental problems by the utilization of waste paper ash (WPA) in the civil engineering field, like using it in mortars and concretes [6,7], supplementary cementing material [8], and bricks [9], as well as using it as a binder to stabilize clayey soils [4,10] or as a potential raw material for mesoporous silica synthesis [11].

The WPA and other similar pulp and paper waste ashes have shown to have few cementitious properties. The composition of WPA can be variant depending on the type, grade, and quality of recycled paper [1]. The major elements present in its chemical composition normally consist of calcium, silicon, and aluminum, as well as some iron and magnesium [4,6,7,12,13]. The compounds present in its mineralogical composition consist of quartz, gehlenite, free lime, calcite, anorthite, and merwinite [4,12]. Bai and Segui [4,12] found that gehlenite together with free lime are the major minerals and give the strongest diffraction pattern.

The WSA has negative and a positive effects in its use as a binder. The first negative effect is that when WSA mixes with water, it leads to expansion, due to hydration of CaO to form $Ca(OH)_2$ [12]. The second negative effect is that WSA has a high porosity that leads to a greater water/binder ratio, penalizing the compressive strength of WSA mortars [14]. Despite its negative effects, WSA has a positive effect when mixing with water, due to it providing a highly alkaline solution. The high alkaline solution leads to the release of more reactive phases like Al_2O_3 and SiO_2, which belong to the WSA or from other cementitious or pozzolanic materials into the system [13,14].

Some studies have shown the possibility of combining WSA with ground, granulated blast-furnace slag (GGBS) in mortars and concretes without incorporating Portland cement (PC) [6,12,13,15]. A concrete mix of 50:50 of WSA/GGBS gained the most strength at the age of 90 days among other ratios of WSA/GGBS blends with a water/binder ratio of 0.5, showing a good match between WSA and GGBS [15]. It was determined that the combination of WSA and GGBS gained better strength because the amount of GGBS diluted the into the system, reducing the amount of expansive material per unit of available pore space. Likewise, by adding GGBS, the water-to-WSA ratio improves, which provides more surface for lime to be adsorbed and interact, therefore providing a better pH environment for a slow hydration material like GGBS [13].

Segui [4] studied WSA as the main binder for stabilizing a clayey soil. The study found that a mixture of WSA and gypsum improves the compressive strength of treated soil samples. It was found that mixing WSA and gypsum in mortars leads to a high amount of ettringite. Nevertheless, the high amount of ettringite did not surpass the maximum requirement of expansion in the soil. Additionally, despite the negative aspects of WSA, the minimum requirements for WSA to be considered as a binder are reached, particularly when mixing the WSA with gypsum. Finally, it was concluded that further studies are necessary for different types of soil.

A soil can be stabilized with either cement or lime. Additionally, to stabilize a soil according Spanish guidelines for roads and bridges (PG3) [16], a minimum of 3 wt % of cementitious material in the soil is necessary. In most cases, adding 3 wt % cement, beside the environmental problems facing consumption of raw materials, and releasing a large amount of carbon dioxide [17–22] leads to a higher strength requirement mentioned in PG3. On the other hand, as mentioned before, the use of WPA as a cementitious material that can fulfill the necessary requirement in civil engineering fields without incorporating the PC can be a great help in reducing the environmental impact of PC, and can diminish the amount of WPA that ends up in landfilled sites.

Consequently, as of today, there is not much research being conducted on entirely replacing conventional cementitious materials like cement or lime and using only recycling paper factory waste to stabilize a soil, hence the present study aims to fully substitute the traditionally used cementitious material. Furthermore, characterizations of raw materials were conducted. Proctor and compressive strength tests, along with slaking and short expansion, were carried out to determine the optimized mixture. Additionally, the long-term expansion and compressive strength was conducted to verify the possible expansion of WPFA and the strength evolution of optimized mixture. Finally, it describes the precautions associated with WPFA and the implementation of the use of WPA as a stable binder in soil, to fulfill the requirement of the Spanish guidelines (PG3) [16] that include 1.5 MPa in compressive strength for a soil type 3, called S-EST3.

4.3. Materials and Methods

4.3.1. Material

4.3.1.1. Cementitious Material (Waste Paper Fly Ash and Cement)

The WPA was supplied by Saica, a Spanish pulp and paper recycling company. The WPA, depending on where it is collected, can be divided into two types: bottom and fly ash. Ashes that are the result of exhausted gases during combustion are commonly known as waste paper fly ash (WPFA), and this is the material used in this work. The size distribution of WPFA was made using a Beckman Coulter laser particle size analyzer (United States).

The density of WPFA was determined using standard UNE 80103 (UNE 80103, 2013). The chemical composition determination of the raw materials was conducted using the X-ray fluorescence method, with a Philips/PANalytical spectrometer, model PW2400.

This study used a powder diffraction technique to identify the crystalline phases in raw materials with a Philips X-ray Diffractometer, with a PANalytical X'Pert PRO MPD Alpha 1 diffractometer, using Cu Kα radiation ($\lambda = 1.5406$ Å, 45 kV, 40 mA). The results were interpreted with EVA using database PDF-2.

This study used a cement type IV/B(Q) 32.5 N (Cem IV) as comparison. It consists of a pozzolanic cement with calcined natural pozzolana (Q), and a resistance class of 32.5 N.

4.3.1.2. Soil

The soil used in this study was provided by Acciona, a Spanish conglomerate group dedicated to the development and management of infrastructure. The soil is collected from an experimental section from a rural area in Zaragoza (Spain) at a depth of 0.5–1.5 m.

4.3.2. Experimental Methods: Specimen Preparation and Testing

4.3.2.1. Slaking in WPFA

As mentioned in standard EN 13282-2 [23], annex A, while working with binders containing free lime as their main composition, it is necessary to carry out the slaking procedure to avoid their possible expansion when performing different tests. As WPFA contains high amounts of free lime, a slaking test is carried out. The slaking procedure was carried out in accordance with EN 13282-2 [23], annex A. This test was conducted with different water/binder ratios. WPFA was mixed with water thoroughly and immediately placed inside the mold, and the temperature output was measured for 24 h using a data logger (Grant 2020 series squirrel data logger, United Kingdom). After 24 h, to verify that the reaction of CaO had totally occurred, to the same mixture 10% more water was added, and the temperature output was measured for another 24 h.

4.3.2.2. Modified Proctor Test

To obtain maximum dry density and optimum water content of the soil, the study carried out the modified Proctor test for the soil—soil with 3% cement and soil with 5% WPFA in dry weight. The modified Proctor test was carried out according to UNE 103-501 [24]. An automatic Proctor compactor from CONTROLS (Italy) was used.

4.3.2.3. Expansion in Stabilized Soil

The procedure of swelling in soils is explained in the European standard EN 13286-49 [25]. The test measures the volumetric expansion in cylindric samples. The test is done by making samples and submerging them into a water bath. After immersing, the samples are measured using a caliper. Generally, the soils analyzed with this method are clayey and provide a good cohesive sample. Applying this method to granular soils causes desegregation of the samples, and it is not useful. Additionally, as mentioned in EN 13286-49 [25], the measurement by caliper makes it impossible to measure expansion correctly over time. Therefore, a homemade experiment was proposed to measure the expansion in soil samples.

The test measures the height change of a confined specimen (soil with WPFA or cement) placed vertically in a mold. The displacement is related to the reactions of cementitious material in the soil samples.

The test contained a circular polyvinyl chloride (PVC) mold with a diameter of 10 cm, a height of 15 cm, and a thickness of 0.5 cm to withstand the lateral forces. The mold had a perforated PVC base attached to the mold with eight screws, in order to make a uniform mold. A paper filter was added to the bottom of the mold to avoid any material loss. Then, a sample soil was ground and sieved through a 16 mm sieve, since the diameter of the mold was 10 cm. The soil is mixed with WPFA and water, and then poured into the mold and compacted in 2 layers with a vibratory rammer (the goal is to reach the density obtained from the modified proctor test). The time of the compaction and water ratio depends on the density obtained from the proctor. After compacting the material, another filter was added to the top layer of the soil. Then, 125 g of small glass spheres with a diameter of 3 mm were added to the mold to have a uniform surface. To simplify the measurement, a metallic mold with a thickness of 0.5 cm was added. To measure the expansion in the mixture, a precise displacement measurement device with six sensors and an accuracy of 0.1 µm is used. The measurement device used was an Ametek solartron model DS/50/G (United Kingdom).

Three of the six sensors were placed on the PVC mold and used as the reference point, and the other three sensors were placed inside the mold, on the metallic plate, to measure the displacement of the material. Figure 1 shows the expansion apparatus used in this study.

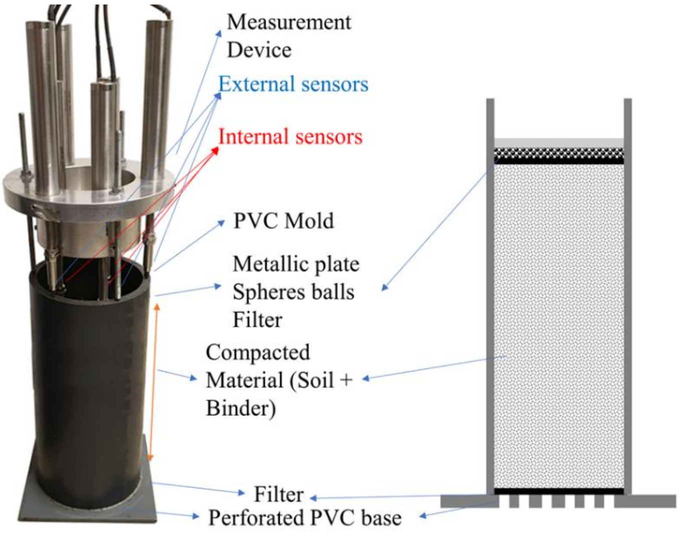

Figure 1. Expansion apparatus.

The test was carried out under seven conditions to measure the expansion in WPFA, as listed in Table 1. In order to compare the effect of water on expansion in stabilized soil, the study tested different water ratios and different delay times. Segui [4] applied a 25 min delay time when fabricating mortars, leading to a better workability; however, in this study, different delay times according to slaking results were used. It should be mentioned that the expansion test was also carried out with soil–cement samples to have a reference. In soil–cement samples, no delay time was applied. After mixing the water with the mixture, it was poured into the mold and compacted.

Table 1. Mixture nomenclature.

Stages	Nomenclature	Water	Delay Time *	Comment
1	T0 W10.5	10.5%	No delay	Obtained from modified proctor test
2	T15 W10.5	10.5%	15 min	
3	T60 W10.5	10.5%	60 min	
4	T0 W8.2	8.2%	No delay	Decreasing water by 2%
5	T15 W8.2	8.2%	15 min	
6	T60 W8.2	8.2%	60 min	
7	T180 W12	12%	180 min	Increasing water by 2%

** Delay time means after mixing the material (soil + waste paper fly ash (WPFA)) with water, it is left to rest (during this time, evaporation is avoided by covering the material with a plastic bag).*

4.3.2.4. Compressive Strength

Spanish guidelines for roads and bridges (PG3, 2014) for a stabilized soil type 3 (S-EST3) requires a minimum of 1.5 MPa in compressive strength at seven days, and a minimum binder content of 3 wt %, which is considered as the amount of cement. Additionally, for stabilized soil with WPFA, the considered amount is 5% by weight of dry soil. Preliminary testing showed that using less than 5% WPFA for stabilization appeared to be insufficient to meet the requirements for PG3 (results not presented here).

To define the optimal mixture, samples were fabricated with different parameters like decreasing the water content, adding different delay times, or curing for a longer period (14 days). Six mixes were proposed to define the optimum mixture. Mix 1 was where the soil is mixed with 5% WPFA and Proctor water content, and cured for 7 days at 20 °C and 90% humidity. The condition in mix 2 was the same as mix 1, except that the samples were cured for 14 days instead of 7 days. In mix 3, the experiment introduced a delay time to the mix. After mixing the soil with WPFA and water, the mixture was set to rest for an hour. Then, it was poured into the mold and compacted. The curing time was considered to be 7 days. The amount of water was considered as Proctor water content. However, in mix 4, the amount of water was decreased. Finally, in mix 5, the amount of water decreased by one point of the Proctor (same as mix 4); however, instead of a one-hour delay time, a 30 min delay was applied. A control mix with cement also was fabricated to compare the result (mix 6). The mixes are shown in Table 2.

Table 2. Mix definitions for compressive strength.

Mix Number	Binder Type/Content	Water Content (%)	Curing Time (days)	Delay Time (min)
Mix 1	5%/WPFA	10.5	7	None
Mix 2	5%/WPFA	10.5	14	None
Mix 3	5%/WPFA	10.5	7	60
Mix 4	5%/WPFA	8.2	7	60
Mix 5	5%/WPFA	8.2	7	30
Mix 6	3%/Cem IV	10.0	7	None

After defining the appropriate mix, the development of strength was studied by manufacturing more samples using mix 5 and curing them for different ages (7, 28, 60, 180, and 360 days). For comparison, samples were made using cement with mix 6 and cured at the same ages as WPFA samples. For each age, four samples were made. A compressive strength test was conducted using a Toni Technik model 2020 (Germany), in accordance with EN 13286-41 [26].

4.3.2.5. Long-Term Expansion Test

Decreasing water in a mix may leave some free lime in the system, which can cause problems in the long term when the mix encounters more water (due to underground or rainwater). To study these scenarios, samples were fabricated and put in contact with water for 180 days, in order to determine the efficiency of delay time and water reduction.

Six samples containing soil–WPFA were prepared, as explained before in Figure 1 but in larger PVC molds (25 cm in height). The water reduction and delay time obtained from previous tests were applied, and samples were made using mix 5. The procedure is as explained in homemade sections, with the difference that the compaction was carried out in five layers (because of the height of the mold and to reach the dry density). Two of the six samples were cured in one day, and the other four were cured for seven days.

After curing, the samples were put in contact with water for 180 days under two conditions. In the first condition, the water was poured from the top of the three samples (one with one day of curing and two with seven days curing) (Figure 2a). In the second case, the remaining three samples (one with one day of curing and two with seven days of curing) were placed in water to absorb by capillary suction in a water bath, as shown in Figure 2b.

To compare the results, samples were made using cement as a binder, according to mix 6, and were put in contact with water over the same period (180 days).

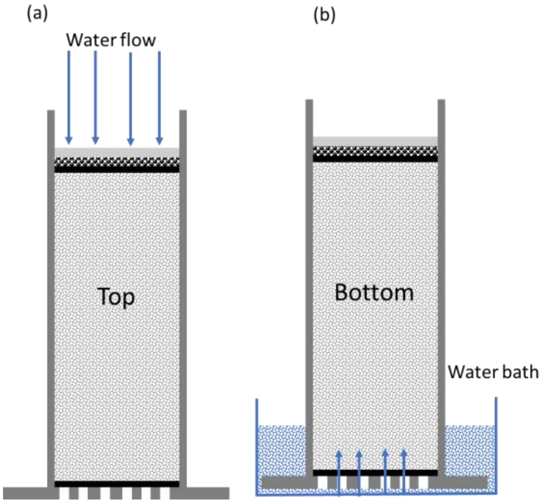

Figure 2. Long-time expansion setup: (a) water flow from top, (b) water suction.

4.4. Results and Discussion

4.4.1. Raw Material Properties

Particle size distribution for WPFA is shown in Figure 3. The WPFA contains uniformly distributed fine particle sizes within the range of approximately 0.05 µm to 120 µm.

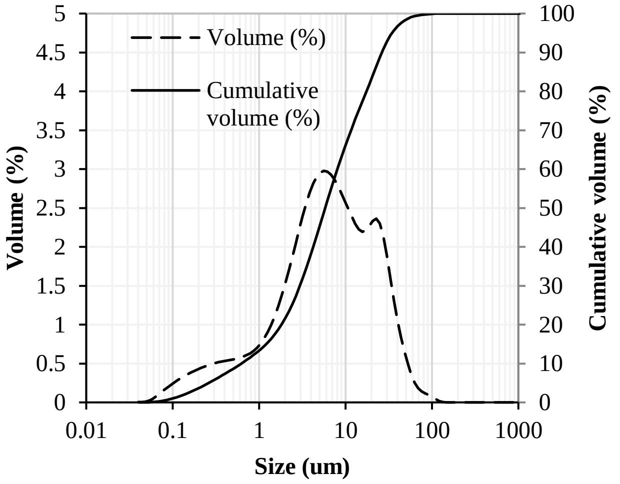

Figure 3. Particle size distribution of WPFA.

The density of WPFA was 2.68 g/cm^3, which is less than the density of the cement (3.05 g/cm^3) and less than that obtained by Segui [14] (2.85 g/cm^3). Its pH was 12.5. The principal elements of WPFA are Ca and Si, with a minor presence of Al, Fe, Mg, and Cl (Table 3). The number of other elements were less than 2%, and a loss of ignition (LOI) of 15.58% was obtained. The free lime content was determined in accordance with EN 1744-1. and 8.0% was obtained.

Table 3. Chemical composition of the raw materials.

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	MnO	K_2O	TiO_2	Cl	Σ Others	LOI
Soil	35.30	27.52	3.75	1.55	0.60	0.97	0.05	0.67	0.21	0.06	0.48	28.24
WPFA	48.86	12.58	12.55	1.01	0.97	1.82	0.03	0.36	1.25	2.33	2.63	15.58
Cem IV	35.55	38.11	10.90	5.59	2.61	1.51	0.05	1.66	0.42	0.06	0.98	2.5

The X-Ray Diffraction (XRD) results showed the presence of calcite, lime, portlandite, quartz, halite, calcium silicate, gehlenite, and aluminum in the WPFA, as shown in Figure 4. Some of the minerals are similar to WSA, like gehlenite, calcite, and lime [4,27,28]. In cement, the presence of calcium silicate, silica, larnite, brownmillerite, tricalcium aluminate, and gypsum have been identified, as shown in Figure 5.

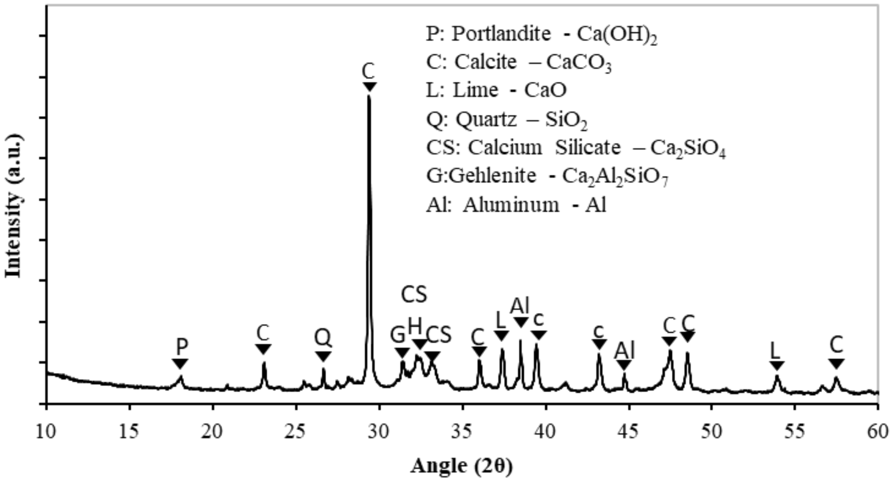

Figure 4. XRD diffractogram for WPFA.

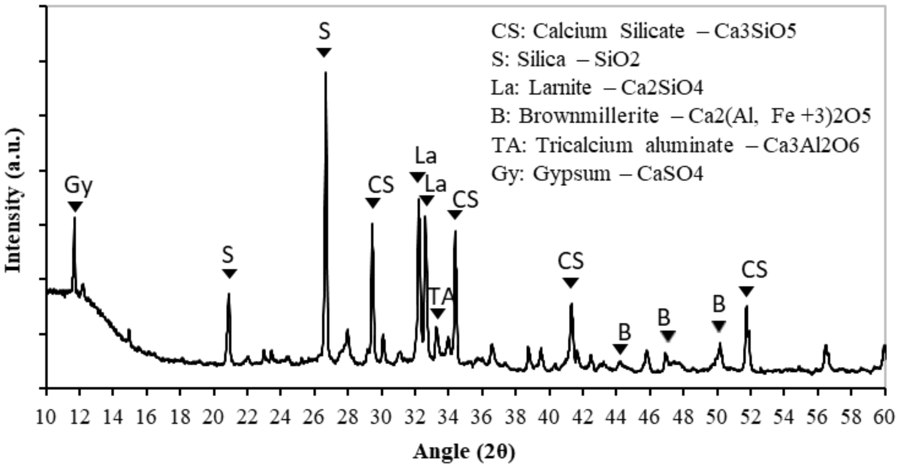

Figure 5. XRD diffractogram for cement IV.

The characterization of the soil is shown in Table 4.

Table 4. Soil characterization.

Test Description	**Test Standard**	**Test Result**
Liquid limit (%)	UNE 103103 [55]	Non-plastic
Plasticity index	UNE 103104 [56]	Non-plastic
AASHTO soil class	AASHTO M145 [57]	A-1-b
Unified soil classification	ASTM D2487 [58]	GM
Free swelling	UNE 103601 [59]	No swelling
Organic matter	UNE 103204 [60]	0.87%
Soluble sulfate	UNE 103201 [61]	0.27%
Optimum moisture (%)	UNE 103501 [62]	10%
pH	EN-12457-2 [63]	11.8

According to the ASTM and AASHTO classification systems, the soil was a GM with silt and sand, and A-1-b showing no plasticity, respectively. The particle size distribution of the soil is shown in Figure 6. The chemical composition is shown Table 3. The mineral phases found in soil are quartz, calcite, albite, biotite, chamosite, and mica.

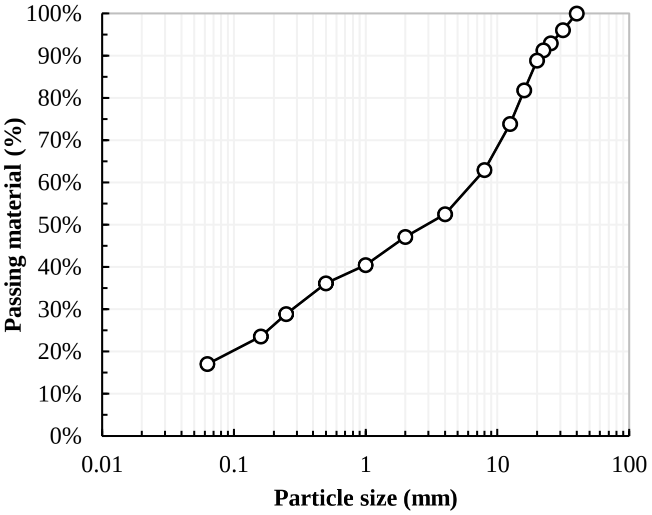

Figure 6. Size distribution of the soil.

Additionally, according to Spanish guidelines (PG3) [16], the maximum allowable amount of organic matter and soluble sulfate must be less than 1.0% and 0.7% by mass, respectively. The organic matter in soil was determined according to UNE 103-204-93 [34], and resulted in 0.87%. The soluble sulfate was 0.27% [35].

4.4.2. Optimum Moisture in the Mix

The modified Proctor test showed that the Proctor curves in soil containing 3% cement were remarkably similar to the soil shown in Figure 7. At its optimum moisture, the density in the soil containing cement was slightly higher than the soil, whereas the soil density obtained from soil containing 5% WPFA was slightly less than that of the soil and soil–cement. Nevertheless, the amount of water increased by 0.5% in the soil with WPFA. When adding WPFA to the soil, due to its high porosity and water demand, it can lead to changes in the optimum moisture and density of the final product.

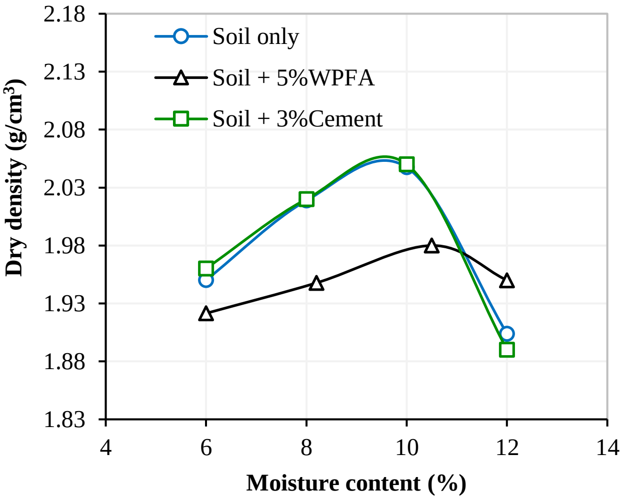

Figure 7. Modified Proctor test.

4.4.3. Slaking Results

The reaction in WPFA while mixing with water leads to a short period of the fast reaction of calcium oxide and heat output, obtaining a temperature increase, as shown in Figure 8a. This fast reaction and heat output last about six hours and tends to reach the ambient temperature. The more water that is added, the higher the heat output, up to a point (40%) where there is more significant amount of water in the system, holding back the release of heat. With 10% water, the maximum temperature reaches at 41 °C, and with 20% around 52 °C, which is the highest among the water ratios. Adding 40% water, the maximum temperatures reaches 42 °C, 1 °C more than 10% water. As soon as the water mixes with WPFA, the temperature rises, and after 30 min the temperature drops significantly; with 10%, 20%, and 40% water, the temperature drops at 38 °C, 40 °C, and 44 °C, respectively. After an hour, the temperature tends to decrease even more, reaching the 32 °C, 35 °C, and 36 °C. As shown in Figure 8a, in the first 15 min the reaction reaches the maximum temperature, and at 30 min, the temperature starts to reduce. Talking into account these results, two delay times of 30 and 60 min were taken into consideration.

While this test was carried out with more water on the following day, by adding 10% water to the same mixtures, it was observed that the slaking in WPFA did not entirely happen in the mixture with 10% water; hence, there was a rise in temperature around 31 °C (Figure 8b). The results showed that there is a minimum water content that allows the total hydration of free lime. If the amount of water is not enough for the free lime to react and hydrate, in the long term, when it comes into contact with more water, it may lead to expansion.

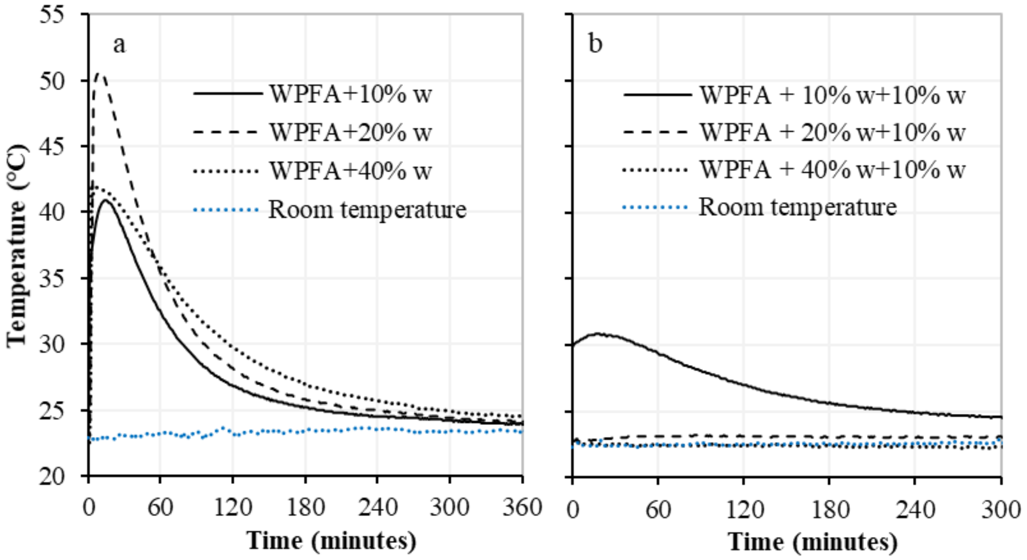

Figure 8. WPFA slaking: first stage (a), second stage (b).

4.4.4. Water Reduction and Delay Time Verification

As the WPFA is very sensitive to the amount of the water, and as free lime reaction is expansive, the homemade test was carried out with different water ratios and delay times. Figure 9a represents the expansion in the mixture with Proctor water content (10.5%) for 0, 15, and 60 min delay times. By adding a delay time, the expansion was decreased significantly, from 0.89% to 0.64% and 0.53% (0, 15, and 60 min delay times, respectively).

Figure 9b shows the result of decreasing the water ratio to 8.2%. The applied delay times were equal to the previous test, and the only variation was the reduction in water by one point of Proctor. The expansion did not exceed the 0.2% in any case: with a 15 min delay, the expansion was around 0.2%, and with a 60 min delay, the expansion was close to zero.

Variation in the quantities of water can be easily generated in a work site, and if they are higher than those of the Proctor, and since WPFA is a material sensitive to the amount of water, special care should be taken. To evaluate this, more water was added to the mix. When adding more water to the mix (12%), even with a 180 min delay, the expansion rose significantly to around 1.5%, as shown in Figure 9c. Even when adding 3 h of delay time, the expansion was still considerable. The results show that WPFA was very sensitive to the amount of water and delay time. Similarly, high water content in a mix is one of the causes of poor strength development, due to an increase in porosity in the WPFA and reduction of the density of the mix.

It should be noted that the test was carried out with a soil–cement sample, and no significant expansion values were obtained (no delay time was applied for cement samples).

As shown, a delay time can reduce the expansion of the mixture by nearly half, and even adding a 15 min delay to the mixture can have a positive effect on samples. Consequently, the water reduction in the mixture leads to even greater decrease in expansion. On the other hand, by adding more water, the expansion, even with a 3 h delay, increases significantly.

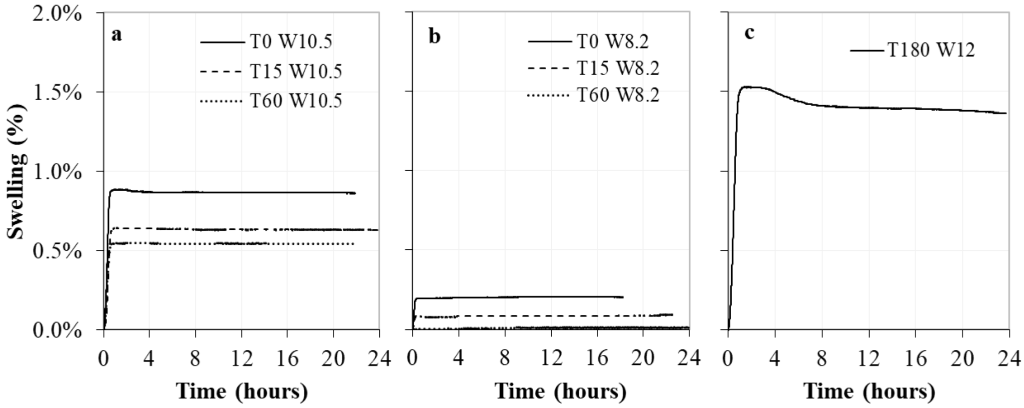

Figure 9. Expansion in soil containing 5% WPFA: (a) Proctor water content, (b) reducing the water content by one point of Proctor, (c) increasing the water content by one point of Proctor.

According to the results of the slaking and expansion, it was observed that a reduction in the amount of water (from 10.5% to 8.2%) reduced the expansion, and by adding a delay time of 60 min, the expansion decreased significantly to nearyl zero. However, in real work scenarios, waiting 60 min may be counterproductive or unusual. Therefore, it was decided to use a delay time of 30 min for the long-term expansion test.

Finally, to verify that the slaking occurred entirely, and see the delay time and water reduction effect over a long period on the stabilized soil, the samples were placed in continuous contact with water for 180 days, and vertical displacement was measured. The samples cured for 1 day are shown in Figure 10a, and in both cases—water absorption by suction or water poured from top—the expansion was less than 0.5%. The results of samples cured for seven days by pouring the water from the top are shown in Figure 10b. The expansion in one of the samples was slightly higher than the other one. However, in both samples it was still less than 0.5%. Finally, Figure 10c shows the 7 days cured sample using water suction. In both samples, the expansion was similar and less than 0.5%. It should be mentioned that Segui [14] found that stabilizing a pretreatment clayey soil by adding 2 wt % quicklime and 6 wt % of a binder containing 80 wt % WSA and 20 wt % gypsum is acceptable in terms of expansion, and no significant expansion were observed.

The results obtained from cement samples did not show any expansion; hence, to avoid confusion, their results are not included in Figure 10.

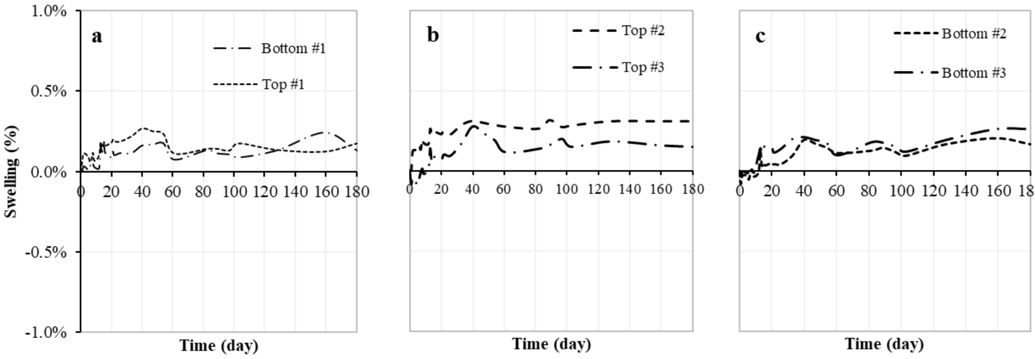

Figure 10. Expansion in stabilized soil after curing for (a) 1 day and (b,c) 7 days.

4.4.5. Strength in Stabilized Soil

The different variable effects, such as delay time, water reduction, and curing time on compressive strength are shown in Figure 11. Results obtained from mix 1 show that adding WPFA to the soil will improve its properties. However, it is not enough for it to fulfill PG3 requirements (1.5 MPa in compressive strength). In mix 2, by curing the samples for 14 days, their strength improved over the second 7 days of curing by 10%. Likewise, adding a one-hour delay time before compaction in mix 3 improved the properties of the soil significantly over mixes 1 and 2 (improved over 50% more than mixes 1 and 2), but it is not adequate to pass the PG3 requirement.

Likewise, by lowering the water content in the mixture and adding a one-hour delay time in mix 4, the strength improved significantly and reached around 2.16 MPa, which is adequate according to PG3. This fact was attributed to the effects of slaking and water reduction in the mix, which led to a better gain in strength. Comparing the results of mix 3 and mix 4, by decreasing the water from 10.5% to 8.2%, the results showed a growth in strength of over 1 MPa. This is believed to be due to how water reacts with WPFA, which besides producing the expansion, makes the mix more porous and causes it to have weak strength in mix 3. In mix 5, instead of an hour delay, a 30 min delay was applied. This decision was made because in practice, a one-hour delay in the job site is counterproductive. This mix showed the best improvement over the other ones by reaching 3.04 MPa in compressive strength. The experiment shows that it is crucial to add a delay time to the mix, and it can improve the strength of the soil. However, the delay time depends on factors like particle size and free lime content in WPFA. On the other hand, because the WPFA hydrates at a fast rate, a delay time of more than one hour should be avoided.

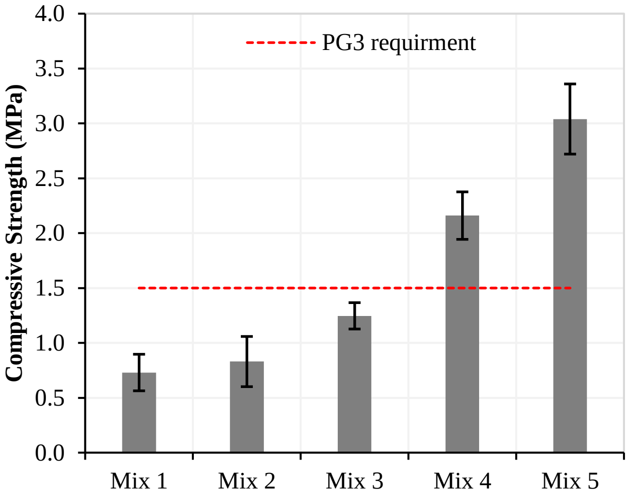

Figure 11. Compressive strength with different conditions.

It was found that applying a delay time of 30 min and reducing the water content by one point of Proctor gained the most strength over other properties. As mentioned by Mozaffari [13], when GGBS is added to the mix, the water-to-WSA ratio improves, showing greater strength. In this case, by reducing the water in the mix by a point of Proctor, it led to improving the water-to-WPFA ratio and gaining more strength.

However, to further study the effect of WPFA and its curing on the samples, the compressive strength test was carried out at different ages, as shown in Figure 12 with the optimum mix (mix 5). The mix gained most of its strength in the first seven days of curing, and in the later ages, from seven days to twenty-eight days, the strength improvement was only 0.18 MPa; it was more or less constant over the other periods (a small variation in compressive strength could be caused by the variability of WPFA properties).

However, in the case of using 3% cement (mix 6), the strength improved over time. As the cement used in this study had pozzolanic materials, the hydration process was slower than normal cement. This type of cement tends to gain a small amount of strength on its first days of hydration, and when the pozzolanic reactions starts, an improvement in strength happens, as shown in Figure 12. Furthermore, the strength in samples with 5% WPFA was nearly equal to cement samples only with a curing time of 7 days, and at the rest of the ages, the cement samples improved significantly, whereas WPFA samples stayed nearly constant.

As it observed in the mineralogical phases of WPFA (see Figure 4), the presence of lime and calcium silicate, which are reactive phases when mixed with water, leads to an increase in strength. Lime present in WPFA hydrates at a fast rate and forms portlandite, giving strength at early ages. At later ages, calcium silicate hydrates due to its slow kinetic reaction, improving the strength by a tiny amount at 14 days.

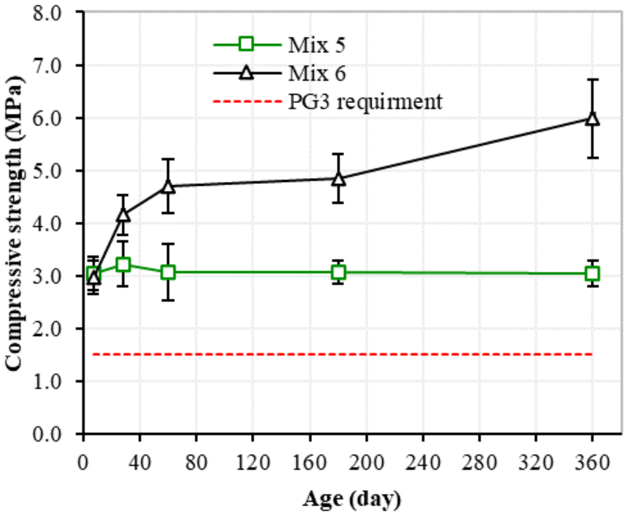

Figure 12. Compressive strength development.

4.5. Conclusions

The process of paper recycling produces a waste that can be used as fuel in waste-to-energy plants. The produced ash in this process is called waste paper ash, and it has been shown to have cementitious properties. In this study, it was verified that it is possible to replace the conventional cementitious binders (cement) with WPFA, fulfilling the mechanical requirement and durability problems relating to possible expansion.

Waste paper fly ash has some cementitious properties, and its chemical composition is mainly composed of calcium, silicon, and aluminum. The mineralogical characterization shows the existence of lime and some reactive phases (calcium silicates), which in the presence of water can react and harden.

However, WPFA has some negative characteristics that penalize its use: (i) when it comes in contact with water, due to the hydration of free lime, it leads to expansion; (ii) excessive water in the mixture penalized the use of WPFA.

The study of slaking, initial expansion and compressive strength tests showed that using WPFA in soil stabilization generates expansion and severely decreases strength. Moreover, a specific study on adding different delay times and water content led to a proposal for optimized conditions for use of WPFA, including adding a delay time and reducing the amount of water.

Moreover, the study of strength development and long-term expansion in WPFA samples showed that strength stayed constant and no significant expansion was observed. This leads to the fact that WPFA is a stable binder in the mixture.

Finally, all the results have shown that use of WPFA as a main binder is well suited for soil stabilization, although care should be taken into account. To avoid possible expansion, a delay time of 30 min is necessary, in conjunction with decreasing the water content in the mixture by a point of Proctor. Furthermore, due to variability in WPFA composition, experiments would be still necessary to confirm these results with other types of WPFA.

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Chapter 5

5.1. Long-Term Comparison between Waste Paper Fly Ash and Traditional Binder as Hydraulic Road Binder Exposed to Sulfate Concentrations

Article title: Long-Term Comparison between Waste Paper Fly Ash and Traditional Binder as Hydraulic Road Binder Exposed to Sulfate Concentrations

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Sulfate attack is one of the drawbacks of cementitious materials for stabilized soils. In the current study, a durability comparison of stabilized soil with cement (Type IV) and waste paper fly ash (WPFA) was conducted. First, the treated soil's unconfined compressive strength (UCS) was tested. Next, the treated soil was subjected to various wetting/drying cycles with various sulfate concentrations and temperatures for a year. In the meantime, samples were taken for DRX, FTIR, and TGA microstructural analyses. Additionally, samples were manufactured to track swelling over an 800 day period. The outcomes show that WPFA's UCS remained constant. Furthermore, ettringite development can be seen in the microstructural studies, however testing on linear displacement over 800 days revealed no significant changes in swelling. Finally, SEM was used to verify the ettringite formation at 360 days in order to confirm the previous findings. All the results indicated that stabilizing soil with 5% of WPFA and 3% of cement IV is possible even in presence of high sulfate concentrations, while maintaining the durability of the structure.

Keywords: waste paper fly ash (WPFA); soil stabilization; sulfate attack; long-term swelling; ettringite formation.

5.2. Introduction

The most common way to stabilize a soil is with the use of binders, such as lime and cement [1–6]. These binders improve the strength and workability of the soils via ion exchange or by forming C–S–H gel and calcium carbonate [4]. One of the disadvantages of using these binders is sulfate attack. Sulfate attack in concrete has been studied vastly in the concrete sector [7–9], and it is well defined as the reaction between sulfate and certain compounds in concrete that leads to the expansion and formation of cracks in concrete. To be specific, sulfate in certain conditions reacts with cement compounds such as monosulfate, portlandite and C–S–H gel. The results of this reaction may be ettringite, gypsum, or thaumasite [10,11].

However, there are two completely different opinions regarding the use of these binders in soils. The first is that these expensive materials in soil are beneficial and can fill up the pores in soil particles, leading to better bonding of soil particles and an improvement of the final strength of soils [12]. The other criticizes the formation of these expansive materials, which may compromise the strength. Needless to say, both of these points of view depend on the generated expansive material, conditions, and sulfate availability in the soil.

One of the sources of sulfate is the soil itself. Soils with some amount of sulfate are quite common all around the world [13]. Gypsum, commonly composed of calcium sulfate dihydrate, is a primary source of sulfate in soils and can be found in gypsiferous soils. As reported by Verheye, gypsiferous soils cover approximately 1 million km2 of the world's surface [14]. Gypsiferous soils can be found in countries in the Middle East (e.g., Iraq, Syria, and Iran) and in Europe (especially in Spain), as well as some parts of North Africa and the USA [15]. According to Jara [16], 7.2% of Spain is covered with gypsiferous soil, mainly located in the eastern part of the country as shown in Figure 1.

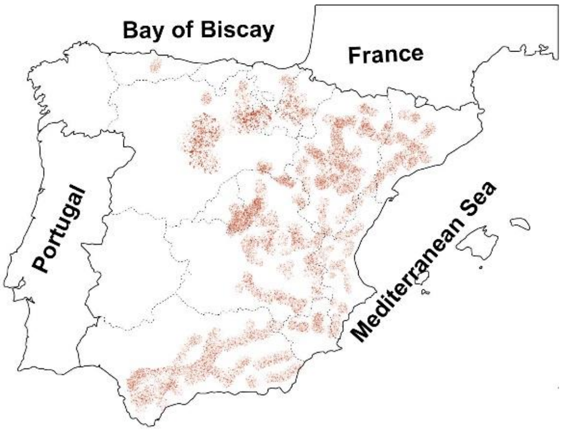


Figure 1. Native gypsum bearing soils in Spain (adapted from [17]).

As mentioned before, the existence of sulfate in soil can be beneficial or problematic due to its reaction with the binder. When lime is added to the soil, cation exchange and flocculation/agglomeration take place almost instantaneously, increasing the pH to around 12. This high pH makes the solution a suitable environment for alumina, silica, and other minerals to react with lime, thereby developing the silica gel (C–S–H) and alumina gel (C–A–H) [3]. The reaction of producing C–S–H and C–A–H are as follows:

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{1}$$

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+}} + 2[\mathrm{OH}]^- \tag{2}$$

$$\mathrm{Ca^{2+}} + 2[\mathrm{OH}]^- + \mathrm{SiO_2} \rightarrow \mathrm{C-S-H} \tag{3}$$

$$\mathrm{Ca^{2+}} + 2[\mathrm{OH}]^- + \mathrm{Al_2O_3} \rightarrow \mathrm{C-A-H} \tag{4}$$

However, two phenomena may occur when the soil or underground water contains some amount of sulfate. The sulfate may react with alumina and form calcium aluminum sulfate hydrates, eventually leading to the formation of ettringite. Undoubtedly, certain parameters must be met in order for ettringite to form, such as a high temperature, a pH above 10, and enough water. All requirements are satisfied when gypsiferous soil is stabilized with cement or lime, except for water, which may come from underground water or rainwater. It should be pointed out that if the pH drops below 10, ettringite formation stops [18]. The ettringite formation process was proposed by Harris et al. [18] as follows:

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+}} + 2(\mathrm{OH})^- \text{ (Ionization of lime; pH rises to 12.3)} \tag{5}$$

$$\mathrm{Al_4Si_4O_{10}(OH)_8} + 4(\mathrm{OH})^- + 10\mathrm{H_2O} \rightarrow 4\mathrm{Al(OH)^{4-}} + 4\mathrm{H_4SiO_4} \text{ (Dissolution of kaolinite at pH > 10.5)} \tag{6}$$

$$\mathrm{CaSO_4} \cdot 2\mathrm{H_2O} \rightarrow \mathrm{Ca^{2+}} + \mathrm{SO_4^{2-}} + 2\mathrm{H_2O} \text{ (Dissolution of gypsum)} \tag{7}$$

$$6\mathrm{Ca^{2+}} + 2\mathrm{Al(OH)^{4-}} + 4(\mathrm{OH})^- + 3(\mathrm{SO_4})^{2-} + 26\mathrm{H_2O} \rightarrow \mathrm{Ca_6[Al(OH)_6]_2} \cdot (\mathrm{SO_4})^3 \cdot 26\mathrm{H_2O} \tag{8}$$

The second phenomenon involves the formation of thaumasite. The sulfate may react with calcium silicate hydrate gel in the system and form thaumasite. The rate of reaction can increase at temperatures below 15 °C. Although ettringite and thaumasite have a similar structural arrangement, the expansive capability of thaumasite is less than that of ettringite as it occupies 45% less volume [19]. Moreover, it was reported that ettringite could expand to as much as two times its original size [20], by 250% [21], or by 137% as calculated using molar volume [19].

In cement hydration, it is believed that this expansion leads to better strength if it happens at an early age. However, if the expansion happens at a later age (delayed ettringite formation), some problems can occur in the structure [22]. It has been reported that the soil expansion does not follow the same rate as Portland cement concrete [19]. The authors of [23] found no significant swelling at the early age. They believed this to be due to the void spaces within the stabilized soil, suggesting greater effects for coarse-grained soil [4]. At a later age, the void spaces inside the soil are filled up, resulting in a more rigid product with fewer pore spaces. Nevertheless, as the ettringite swells and no more pore spaces are left to fill, the swelling pressure is applied to other parts of the structure and can lead to potential catastrophe [23]. One example was reported by Chen et al. [24], where an 8.8 mile section of a road in Texas, USA, which was treated with lime, was damaged and caused 12.7 million USD worth of damage.

Nevertheless, ettringite formation does not only depend on sulfate content [19,25], and is not always expansive. It depends on many factors such as composition, curing period time and temperature, water availability, reactive phase availability [23,25], compatibility with other cement phases [9], and amount of lime. Studies have reported that the swelling potential of sulfate-rich soils is decreased when they are treated with low C3A binders such as ground granulated blast furnace slag (GGBS) [26]. Seco et al. [27] found that stabilization with a byproduct from the calcination of natural MgCO3 rocks (defined as PC-8) could significantly decrease swelling while maintaining a similar or better strength compared to stabilization with lime. Eyo et al. [28] conducted a study using RoadCem (RC), an additive for nanotechnology manufacturing. It was concluded that using 1% RC and replacing cement with GGBS could decrease the swelling. Fly ash geopolymer has also been shown to be a viable solution by increasing pozzolanic reactions [29]. However, it requires supplemental additives. The use of fly ash, particularly low-calcium fly ash, can reduce the rate of heat evolution and the magnitude of the temperature rise in concrete, especially at high replacement levels. Another way to reduce swelling, at least for soil treated with lime, is mellowing [18,30]. It has been shown that mellowing can significantly decrease swelling and double the sulfate content.

Another important factor influencing the structure and strength of stabilized soils in cold regions is represented by freeze–thaw cycles [31]. Yan et al. [32] investigated the characteristics of unconfined compressive strength and pore distribution of lime–fly ash loess mixtures under freeze–thaw cycles and drying–wetting cycles through a series of experiments in the laboratory. The authors showed that the freeze–thaw cycles caused frequent phase changes and water transference in samples, which continuously lowered the friction and bite forces between the soil particles, eventually leading to lower strength.

Waste paper ash (WPA), a byproduct of recycling paper, varies in terms of its chemical and physical properties, generally depending on the raw material used during incineration. However, in most cases, WPA contains cementitious properties [33,34] and, to some extent, follows the same pattern as cement. After mixing WPA with water, lime makes the solution alkaline (around 12) [35].

In the previous study, the usability of WPFA as a binder was discussed [35]. In summary, WPFA was successfully used as the sole binder to stabilize the given soil. However, the durability of WPFA in the presence of a sulfate source was not considered. The study of the durability of WPFA is essential because of the similarities between WPFA and cement. Similarly to cement, WPFA in the presence of sulfate could swell and eventually lead to structural damage.

Moreover, swelling in soils by the formation of ettringite depends on many factors such as temperature, water and sulfate content, and time [23,25]. Therefore, this paper studies the long-term effect of soil stabilized using WPFA in the presence of different sulfate concentrations, by means of measuring the mechanical performance and swelling. The study valued mineralogical changes using XRD, thermogravimetry analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analyses. For this purpose, all tests were conducted in different conditions (at 5 °C and 20 °C with different sulfate solutions), and the results were compared with a commonly used binder (CEM IV). This study's findings will further reveal the usability of WPFA as a binder even in a harsh environment and would be a major importance in assessing WPFA in comparison with traditional cement.

5.3. Materials and Methods

5.3.1. Soil, Stabilizers, and Reagent

The treated soil was collected from the suburbs of the city of Zaragoza, Spain (north of Spain), where the metropolitan area is predominantly composed of soils contaminated with sulfate. Given the low load-bearing capacity of these soils due to their physical–mechanical properties, they are not used in construction work; thus, the stabilization of soils with cement materials is a practical solution. The goal was to stabilize a 30 cm layer of this soil. Upon further inspection, the subgrade soil (below the treated soil, around 0.5 m depth) showed a high amount of sulfate concentration (1.4% according to EN 103201). Hence, the study also considered the underlying soil. The properties of tested soils such as particle size distribution, liquid limit, plastic limit, sulfate content, and pH values are shown in Figure 2 and Table 1.

Table 1. Properties of the tested soils.

Test Description	**Test Standard**	**Test Result**	
		Soil	**Subgrade Soil**
USCS soil classification	ASTM D2487	GP–GM	SP–SM
Liquid limit (%)	UNE 103103	Non plastic	Non plastic
Plasticity index	UNE 103104	Non plastic	Non plastic
Free swelling	UNE 103601	No swelling	No swelling
Organic matter	UNE 103204	0.87%	1.0%

Soluble sulfate	UNE 103201	0.27%	1.4%
Optimum moisture (%)	UNE 103501	8.2%	7%
pH	EN-12457-2	11.8	8.11

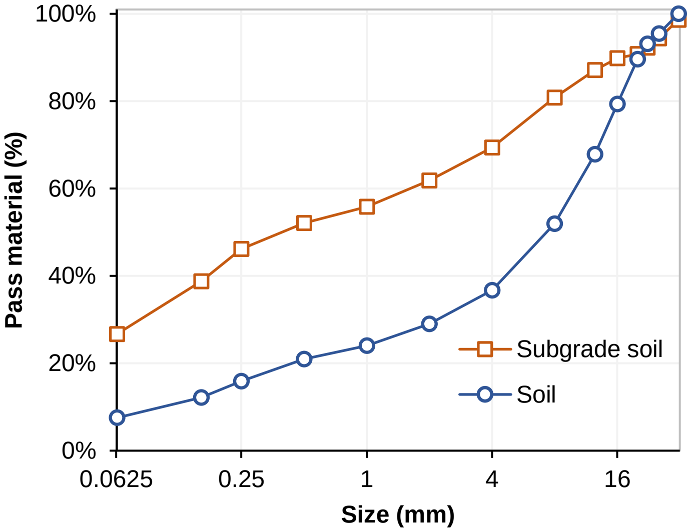


Figure 2. Particle size distribution of soils.

The stabilizers included a pozzolanic Portland cement (CEM IV B(Q) 32.5 N) and WPFA. The cement consisted of a pozzolanic cement with additional calcined natural pozzolana (Q) and a resistance class of 32.5 N; and the waste paper fly ash was derived from paper manufacturing. The WPFA studied in this study was supplied by Saica (Sociedad Anonima Industrias Celulosa Aragonesa), a Spanish pulp and paper manufacturer that uses only recycled paper as raw material.

The chemical composition of all raw materials (both soils and stabilizers) was determined by X-ray fluorescence, using a Philips/PANalytical spectrometer, model PW2400. The main elements in both soils were calcium and silicon. The main elements in WPFA and cement were calcium, silicon, and aluminum. There were some traces of magnesium and chlorine in WPFA, as shown in Table 2.

Table 2. Chemical composition of raw materials.

Chemical Composition	**Mass Fraction (%)**			
	WPFA	**Cement IV**	**Soil**	**Subgrade Soil**
CaO	48.86	35.33	35.3	38.74
SiO_2	12.58	38.11	27.52	18.34
Al_2O_3	12.55	10.9	3.75	3.23
MgO	1.82	1.51	0.97	0.88
Fe_2O_3	1.01	5.59	2.17	1.55

ClO	2.28	-	0.06	0.04
TiO_2	1.20	0.42	0.21	0.17
SO_3	0.96	2.61	0.6	2.84
P_2O_5	0.8	2.72	1.14	1.10
Other	1.6	-	-	-
LOI	17.8	2.5	28.2	33.1
Free lime content	6.36	-	-	-
Density (g/cm^3)	2.68	3.00	-	-

Figure 3 shows the particle size distribution of PC and WPFA. The as-received WPFA contained particles with a d_{50} of ~6.4 µm, whereas the cement contained particles with a d_{50} of 11.8 µm, showing a far coarser particle size than WPFA.

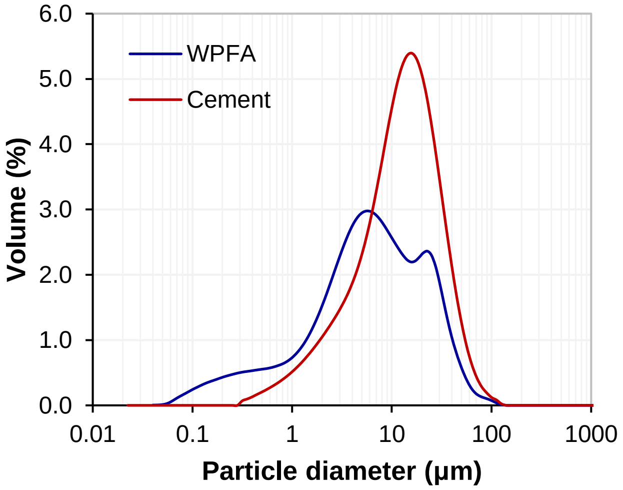


Figure 3. Particle size distribution of WPFA and WPBA.

This study applied the powder diffraction technique to identify the crystalline phases in soils and stabilizers using a Philips X-ray diffractometer with a PANalytical X'Pert PRO MPD Alpha 1 diffractometer using Cu Kα radiation (λ = 1.5406 Å, 45 kV–40 mA). The results were interpreted using EVA software (database PDF-2).

The presence of calcite, lime, quartz, larnite, aluminum, and halite was recorded in WPFA, as shown in Figure 4. Moreover, a tiny amount of portlandite could be found due to moisture in the environment. The minerals presented in cement were quartz, calcite, mayenite, brownmillerite, gypsum, tricalcium aluminate, larnite, and calcium magnesium aluminum oxide silicate. The soil and subgrade soil were composed of quartz, calcite, albite, biotite, chamosite and mica, as shown in Figure 5.

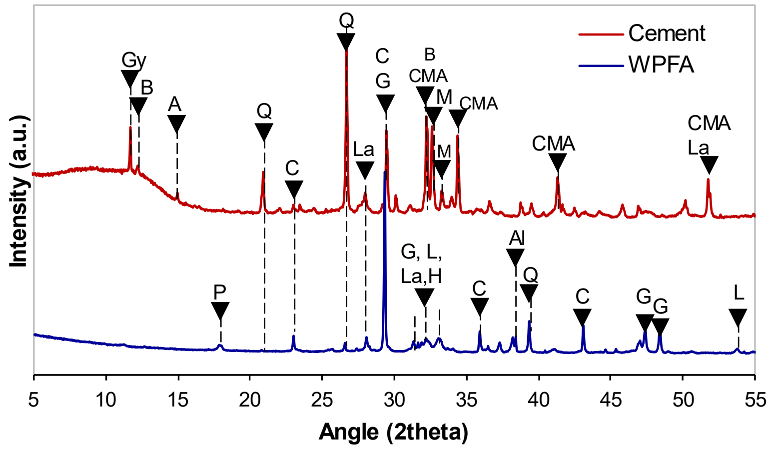


Figure 4. Diffractograms of WPFA and cement. Gy: gypsum, B: brownmillerite, A: albite, Q: quartz, La: larnite, M: mayenite, P: portlandite, C: calcite, L: lime, G: gehlenite, H: halite, CMA: calcium magnesium aluminum oxide silicate, A: aluminum.

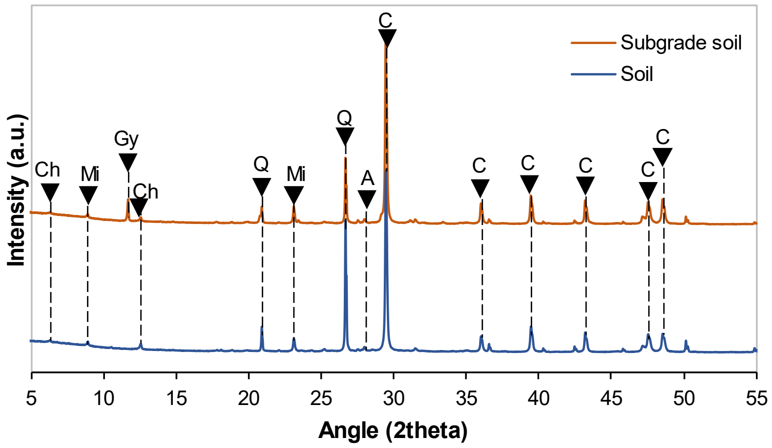


Figure 5. Diffractograms of soil and subgrade soil. Gy: gypsum, A: albite, Ch: chamosite, Q: quartz, Mi: mica, C: calcite.

Moreover, in addition to these materials, calcium sulfate 2-hydrate ($CaSO4·2H2O$) from Panreac was used as a reagent. It was mixed with water in order to facilitate sulfate attack of the test specimens. The amount of calcium sulfate is described in Section 2.3.

5.3.2. Sample Preparation

The studied soil was part of an experimental trial, located in Villamayor de Gállego, a small village near Zaragoza, Spain. The goal was to treat the soil for heavy traffic usage, whereby a minimum of 2.5 MPa according to the unconfined strength test (UCS) was required at 7 days in this case. Table 3 shows the test design parameters such as the binder content and UCS for both soil + WPFA and soil + cement.

Table 3. Test design parameters for soil stabilization.

	Soil + WPFA	**Soil + Cement**
Binder content (wt of soil)	5%	3%
Water content	8.2%	7%
Modified proctor density	1.98 g/cm^3	2.05 g/cm^3
UCS at 7 days	3.04 MPa	2.98 MPa
Applied delay before compaction	30 min	-

5.3.3. Procedure for Measuring Swelling

An in-house experiment was designed to characterize the effect of swelling under sulfate attack on stabilized soils in the long term. The experiment measured one-dimensional swelling/shrinkage in the vertical direction of a confined specimen. This allows more flexibility and a greater experimental duration without damaging the sample. PVC molds were fabricated a thickness of 0.5 cm, height of 20 cm, and diameter of 10 cm. As the base, perforated PVC was also used, with a thickness of 0.5 cm. The base and the mold were glued together using eight screws.

The preparation of soil consists of grinding the soil to obtain a maximum particle size of 16 mm. The soil was weighed and mixed with binder (either 5 wt.% WPFA or 3 wt.% cement) and water according to Table 3. After mixing thoroughly, the mix was then poured into the mold in five layers and compacted. For samples with WPFA, after mixing with water, a 30 min delay was considered before pouring and compacting. This delay time allowed the WPFA to gain better workability and performance and as well as reduced swelling to some extent. After fabricating the samples, a 125 g sphere was added to level the top layer of the soil. Finally, to facilitate measurements, a metallic plate was added to the top of the samples. For clarity, a schematic of the mold is shown in Figure 6.

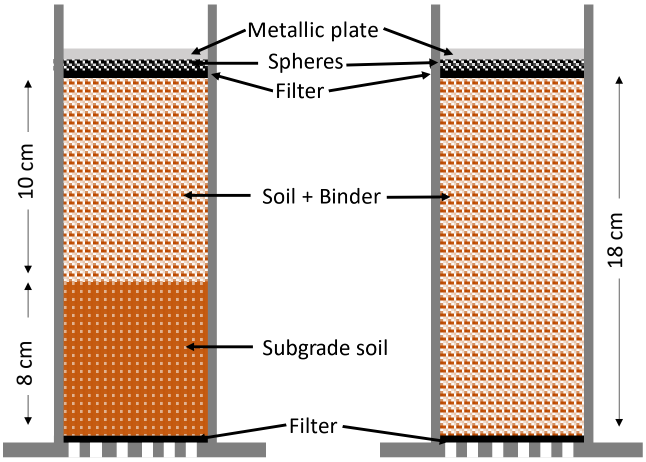


Figure 6. Schematic of swelling sample.

After fabrication, the samples were cured for 7 days. In total, 36 samples were fabricated. Two temperatures were considered (5 °C and 20 °C). To determine the effect of sulfate on the samples, three sulfate solutions were considered. In the first (W1), only tap water was used. For the second batch (W2), the samples were fabricated using subgrade soil to determine the effect of underlying soil on the stabilized soil. Additionally, to avoid any loss of sulfate concentration from subgrade soil to the water bath, 2.5 g/L calcium sulfate was added to the water bath. Lastly, for the third batch (W3), 20 g/L calcium sulfate was added to the water bath. Each experiment for WPFA (in terms of water batch and temperature) was conducted in quadruplicate, whereas experiments with cement were conducted in duplicate. Due to the lack of research and the possible greater heterogeneity on the behavior of WPFA exposed to sulfate concentrations, more samples were manufactured. Table 4 shows the number of samples and the wetting/drying conditions for each sample batch.

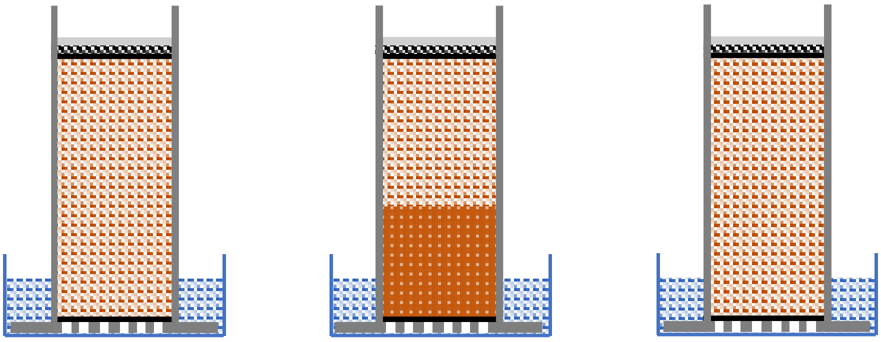
Table 4. Confined swelling samples with different conditions. S: soil, Sg: subgrade soil, F: WPFA, C: cement.

Number of Samples	Samples	Wetting/Drying Condition
4	S + F + W1	20 °C/95% RH
4	S + F + W1	5 °C/dry
4	Sg + S + F + W2	20 °C/95% RH
4	Sg + S + F + W2	5 °C/dry
4	S + F + W3	20 °C/95% RH
4	S + F + W3	5 °C/dry
2	S + C + W1	20 °C/95% RH
2	S + C + W1	5 °C/dry
2	Sg + S + C + W2	20 °C/95% RH
2	Sg + S + C + W2	5 °C/dry
2	S + C + W3	20 °C/95% RH
2	S + C + W3	5 °C/dry

The wetting/drying cycles were carried out immediately after day 7. The samples were placed inside a designated water bath for 1 week, and 2 weeks to dry. This cycle was repeated for 800 days. After each cycle, the weight and the swelling were measured.

A precise displacement device was used to measure the swelling/shrinkage in the soil samples as described in previous work [36].

Samples were placed in a water bath at 20 °C, and 90 ± 5% humidity, or at 5 °C. The water level was maintained around 1.5 ± 0.5 cm above the samples to allow the water to be drawn up into the sample via capillary action. Figure 7 shows a schematic view of wetting portion with different sulfate solutions.



Water 1
Tap water
Soil + Binder (WPFA or Cement)

Water 2
Subgrade soil + Soil + Binder (WPFA or Cement)

Water 3
20 g/L sulfate
Soil + Binder (WPFA or Cement)

Figure 7. Water bath and different sulfate solutions.

5.3.4. Microstructural Studies of Stabilized Soil

To study the behavior of the soil stabilized with binders, 100 g of soil was ground to a particle size of 63 µm. Later, it was mixed with 5% WPFA or 3% cement and the three different solutions mentioned in the previous section (W1: tap water, W2: containing underlying soil, W3: containing 20 g/L sulfate). After mixing thoroughly, it was poured into a container and left to cure at two different temperatures (5 and 20 °C). This experiment was conducted to accelerate the hydration process and promote the appearance of the other phases such as ettringite or thaumasite.

The hydration of the samples was stopped at different curing ages (30, 180, and 360 days) using the solvent exchange method. Then, the samples were pulverized for characterization by XRD, thermogravimetry analysis (TGA), scanning electron microscopy (SEM), and FTIR. For TGA, a Mettler Toledo model TGA/DSC 1 Thermal Analyzer was used with 10 µg of material at temperatures within the interval 30–1000 °C, N2 flow of 50 mL/min, and a heating rate of 10 °C/min. Before each test, the samples were stabilized at 100 °C for 15 min. A Frontier FTIR spectrometer (Perkin Elmer) was used to acquire 16 scans with a spectral resolution of 4 cm^{-1} over a range of 4000–400 in attenuated total reflection (ATR) mode.

Scanning electronic microscopy (SEM) images of soil stabilized with WPFA or cement at 360 days were obtained to verify the formation of ettringite, using a FEI scanning electronic microscope equipped with an energy-dispersive X-ray microscopy device model ESEM Quanta 200, XTE 325/D8395.

5.3.5. Unconfined Compressive Strength

To evaluate the changes in strength of the stabilized soil under sulfate attack, a UCS test was carried out. The samples were prepared in accordance with EN13286 and cured for 7 days at 90 ± 5% RH. Then, the samples were placed inside a tray, and the water solution (W1, W2 or W3) was poured into the tray. For this test, the samples were exposed to the solution for 1 week, and then left to dry at room temperature for 2 weeks. The experiments were carried out over a 1-year period, and then the compressive strength test was performed.

5.4. Results and Discussion

5.4.1. Unconfined Compressive Strength

Figure 8 shows the results of the unconfined compressive strength (UCS) test cured at different ages in an optimum environment (90 ± 5% RH, and 20 °C) for soil stabilized with WPFA or cement. In the case of soil treated with WPFA, the UCS tended to stay nearly constant, obtaining the maximum value over a short period of time (3 MPa at 7 days) compared to cement samples. Moreover, as the cement was pozzolanic, its strength doubled over the 1-year period.

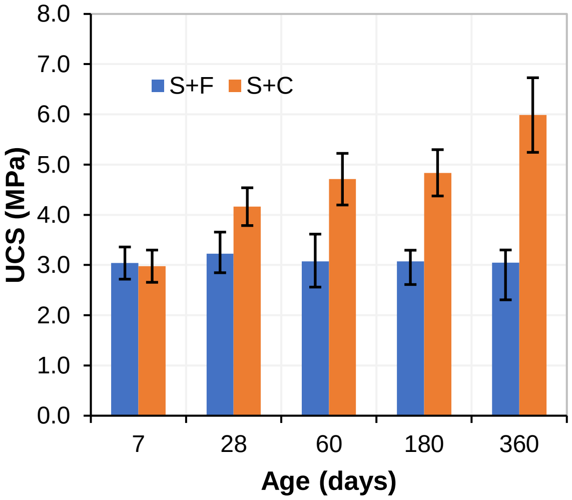


Figure 8. UCS for soil stabilized with WPFA or cement.

Figure 9 shows the results of the unconfined compressive strength (UCS) test for soil stabilized with WPFA or cement at 360 days under different conditions. The first part shows the samples cured in a humid room (at 20 °C, with 90 ± 5% humidity), while the second and third parts show samples subjected to the above-described wetting/drying cycles for 1 year.

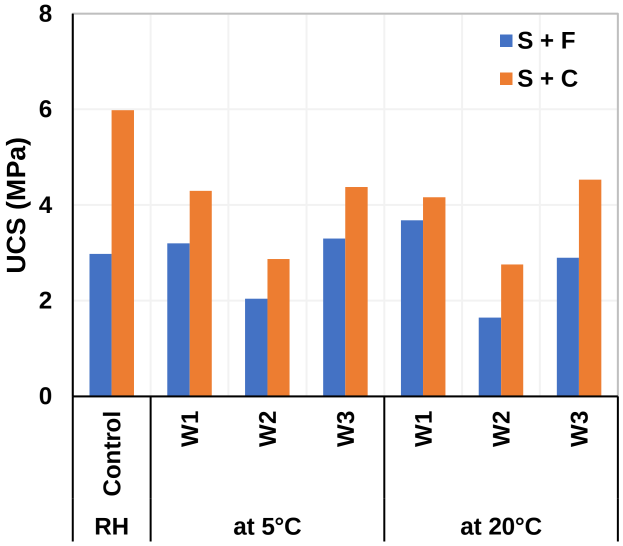


Figure 9. UCS at 360 days for soil stabilized with different binders, temperatures, and sulfate solutions.

At first glance, the strength of the WPFA samples remained fairly constant across all conditions (~3 MPa) for W1 and W3. This is due to the fact that WPFA gained most of its strength in the first 7 days of curing as shown in Figure 8. However, for samples exposed to W2, a decrease of 31 to 45% was observed. This decrease can be justified with the fact that only a portion of the sample (only 10 cm) was stabilized, and no treatment was applied to the subgrade soil.

In the case of cement samples, a significant decrease from 5.98 MPa to ~4.3 MPa (a decrease of 28%) was observed following the wetting and drying cycles. Furthermore, this decrease remained unaffected by the various sulfate concentrations. Additionally, the strength of cement samples exposed to W2 decreased, similarly to WPFA samples, because only 10 cm of this sample was treated.

There are two possible explanations for the decrease in strength in cement samples. The cement used in this study was pozzolanic and was, thus, characterized by lower strength gains at an early age. The cement samples reached 50% strength after 7 days compared to that after 360 days. Moreover, since the samples were subjected to wetting/drying cycles, during the drying period, the cement did not completely develop in terms of hydration reactions and strength. Likewise, due to these wetting/drying cycles, internal cracks may have been produced inside the material, which would have affected the final resistance.

5.4.2. Swelling in Treated Soil

The average confined swellings and weight changes at 800 days are shown in Table 5. The swelling of samples showed no significant changes during the 800 day period. The greatest change was recorded for the soil stabilized with WPFA and tap water at 20 °C with a value of 0.15%, showing a small amount of shrinkage in the sample. For cement samples, the greatest change was recorded to the soil stabilized with cement and water with 20 g/L sulfate content at 20 °C with a value of −0.11%. Both WPFA and cement samples exhibited a small amount of shrinkage. Moreover, samples at 20 °C showed more shrinkage than those at 5 °C. Nevertheless, these values were too small to affect the properties of the samples.

Table 5. Average confined swelling and weight changes. S: soil, Sg: subgrade soil, F: WPFA, C: cement.

Specimen Type	Average Swelling Changes	Average Weight Changes
S + F +W1 (5 °C)	−0.14%	1.44%
Sg + S + F + W2 (5 °C)	−0.06%	0.30%
S + F + W3 (5 °C)	−0.03%	1.78%
S + F + W1 (20 °C)	−0.11%	1.84%
Sg + S + F + W2 (20 °C)	−0.10%	0.73%
S + F + W3 (20 °C)	−0.08%	1.96%
S + C + W1 (5 °C)	−0.05%	0.44%
Sg + S + C + W2 (5 °C)	−0.02%	0.19%
S + C + W3 (5 °C)	0.02%	0.02%
S + C + W1 (20 °C)	−0.05%	1.23%
Sg + S + C + W2 (20 °C)	−0.09%	0.40%
S + C + W3 (20 °C)	−0.11%	0.80%

Another point is that the weight of the samples was also increased following the drying/wetting cycles. The maximum weight changes were recorded for the soil stabilized with WPFA and W3 at 20 °C (1.96%) and the soil stabilized with cement + W1 at 20 °C. Figures 10 and 11 show the changes in each sample (SG + S + F + W2 and SG + S + C + W2) over the 800 days, as well as their average weight. For the sake of saving space, the remaining figures are presented in Appendix A.1.

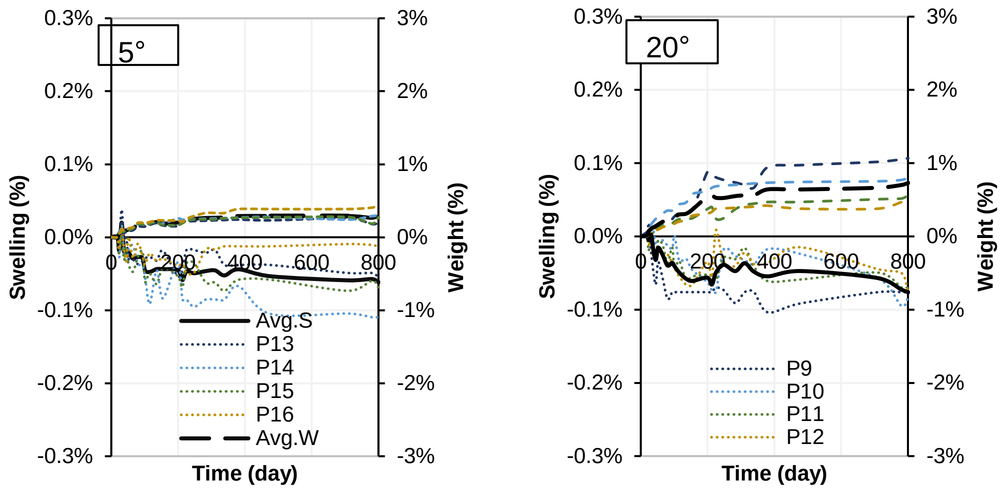


Figure 10. Swelling results in Sg + S + F + W2 at different temperatures.

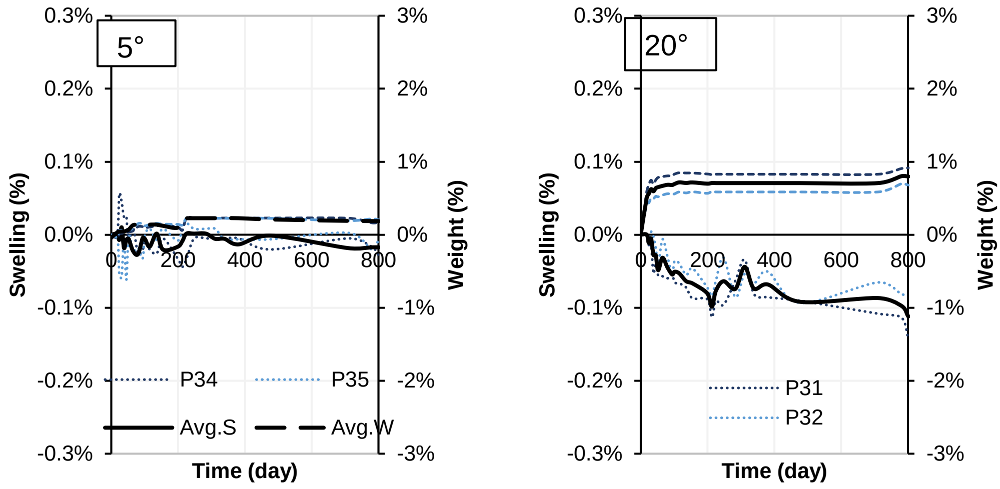


Figure 11. Swelling results in Sg + S + C + W2 at different temperatures.

5.4.3. Microstructural Studies of Treated Soil

The mineralogical compositions of the soil samples stabilized with cement or WPFA for 30, 180, and 360 days are shown in Figures 12–17. Most of the peaks identified were similar in all the cases, corresponding to soil and subgrade soil, and no significant changes were observed during the 1-year period. For the sake of clarity, only a portion of each figure (from 5°–20° 2θ) is shown to observe the evolution of AFt–AFm and gypsum in the system.

For samples stabilized with W1 and W3, very little ettringite was formed, and the maximum peak was reached after 180 days. However, at 360 days, the amount of ettringite decreased for both WPFA and cement samples. For samples containing subgrade soil, the gypsum peak at 11.61° (2θ) was lowered, indicating the consumption of gypsum, while the formation of ettringite increased to its maximum peak after 180 days. At 360 days, there were still some traces of gypsum in the system, and the ettringite peaks were reduced. The variation in temperature did not play an essential role in the formation of thaumasite or other phases.

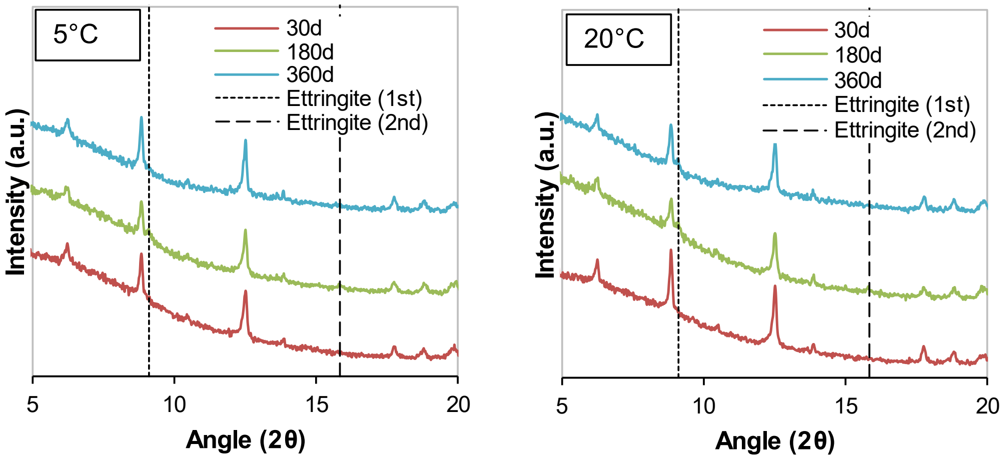


Figure 12. Diffractograms of S + C + W1 at different temperatures.

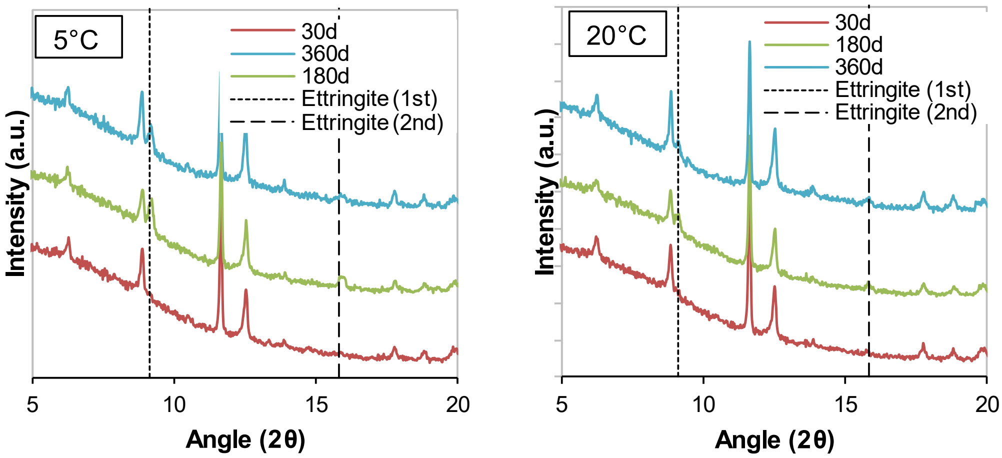


Figure 13. Diffractograms of Sg + S + C + W2 at different temperatures.

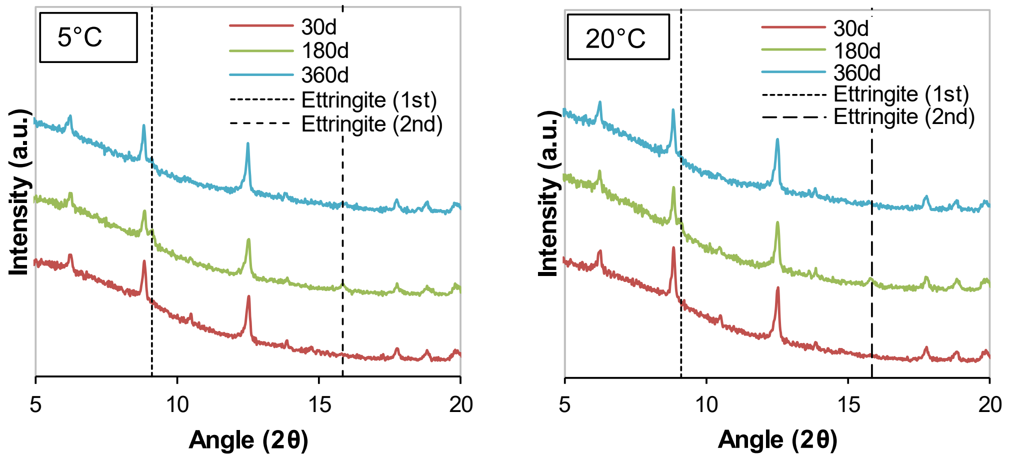


Figure 14. Diffractograms of S + C + W3 at different temperatures.

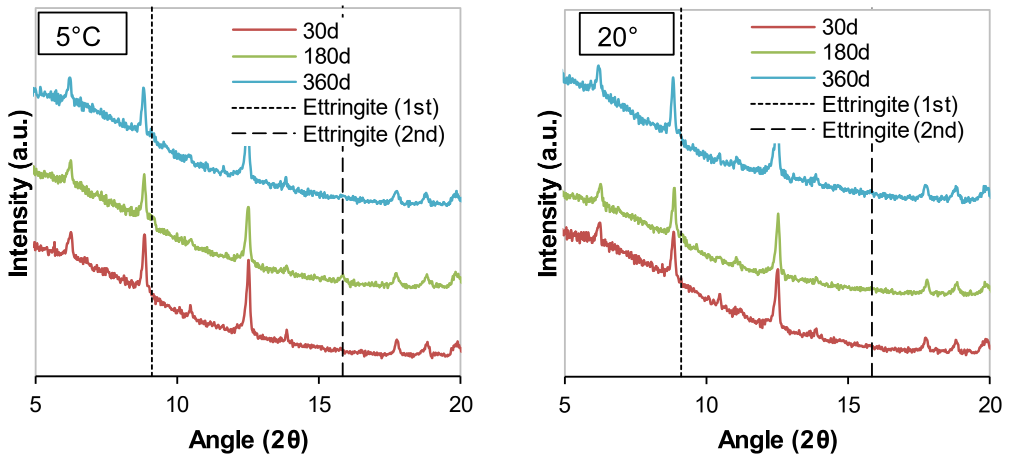


Figure 15. Diffractograms of S + F + W1 at different temperatures.

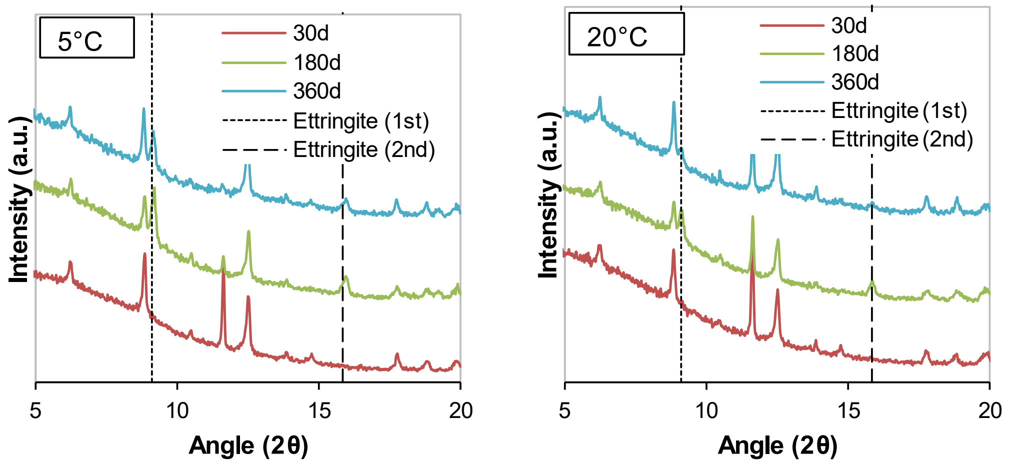


Figure 16. Diffractograms of Sg + S + F + W2 at different temperatures.

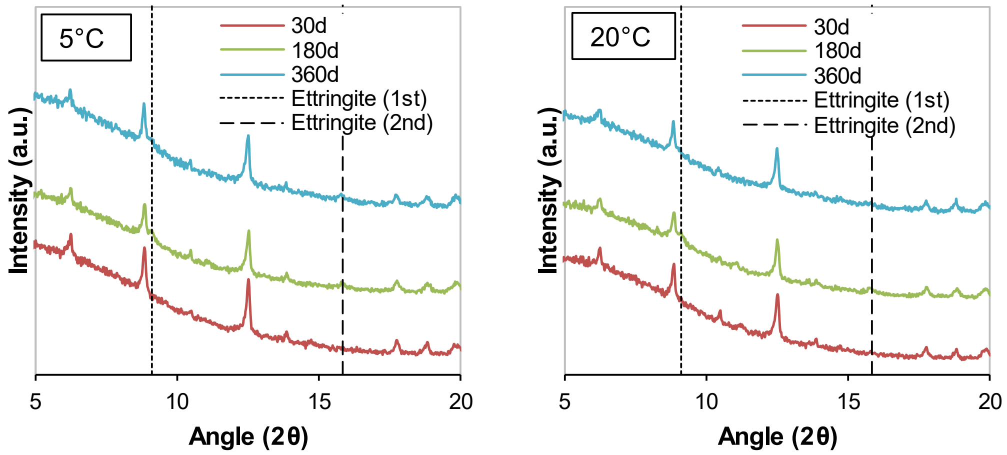


Figure 17. Diffractograms of S + F + W3 at different temperatures.

TGA analysis was conducted to compare the results of the samples with different hydration ages, different sulfate concentrations, and different temperatures. The major peak was related to calcite at 731 °C, originating from the soil and binder, which remained the same throughout the hydration. Unfortunately, the TGA results did not provide an accurate measure of phases other than calcite. Due to space limitations, only one figure is presented for each binder (Figures 18 and 19), i.e., subgrade soil and soil with each binder at temperatures of 5 and 20 °C; the remaining figures are presented in Appendix A.2. The results indicated that there were no major changes as a function of hydration age or sulfate concentration. These results also indicated that the amount of binder was insufficient (5 wt.% WPFA or 3 wt.% cement) to affect the system significantly.

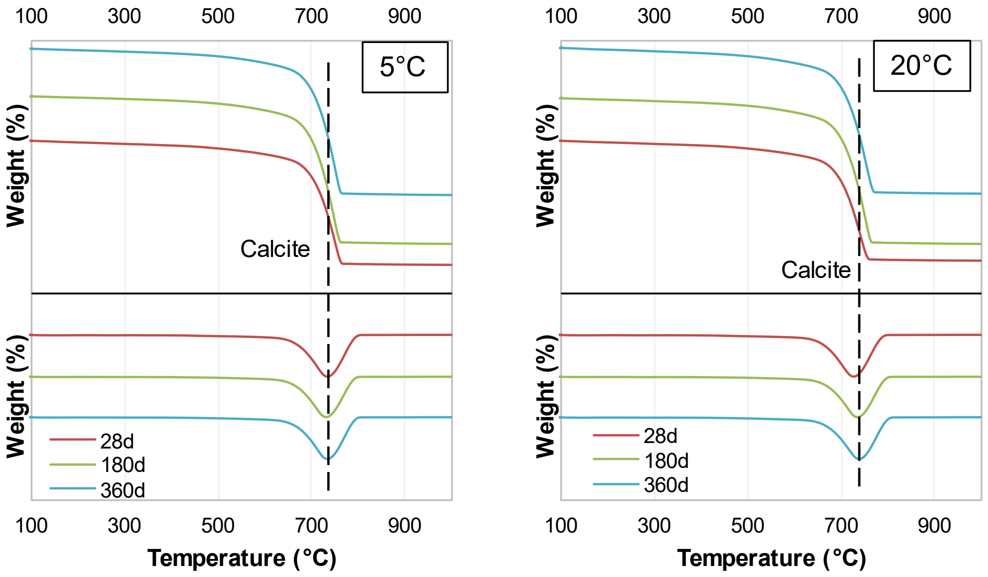


Figure 18. TGA traces of Sg + S + F + W2.

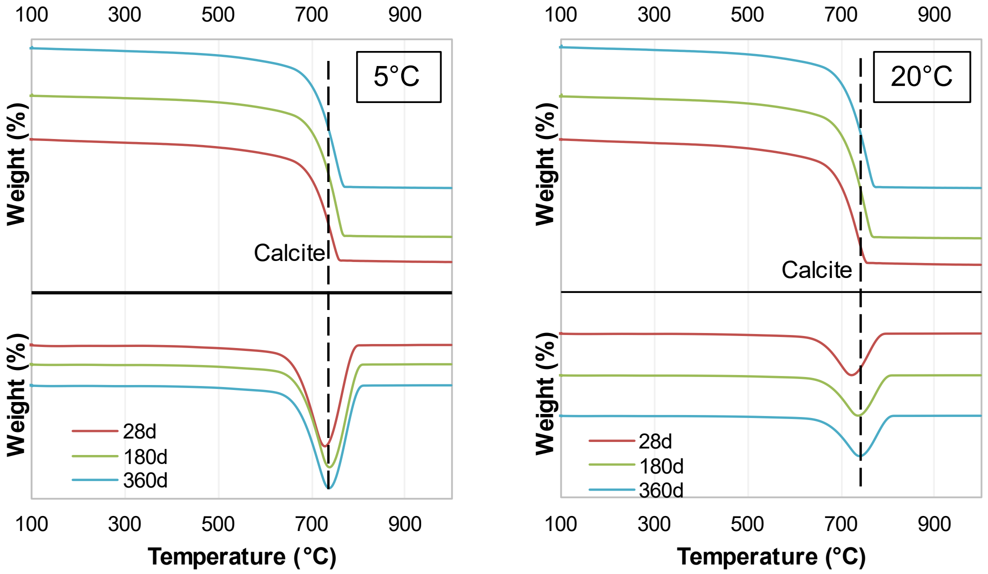


Figure 19. TGA traces of Sg + S + C + W2.

Figures 20 and 21 show the FTIR spectra for the soil stabilized with WPFA or cement at curing ages of 30, 180, and 360 days. Table 6 provides the analyses of FTIR spectra for the soil stabilized with WPFA or cement. The similarities in the FTIR spectra confirmed the quite similar reaction products formed for both cement and WPFA. The absorption bands at 712 cm^{-1}, with a narrow band around 875 cm^{-1} and a strong band at 1420 cm^{-1}, were assigned to the asymmetric stretching vibration of C–O bonds of calcite. The absorption bands at 470 and 525 cm^{-1} could be assigned to the bending vibration of Si–O [37]. Moreover, the small peaks at 604 and 671 cm^{-1} were assigned to the stretching and bending modes of sulfate. The two small bands at 780 and 800 cm^{-1} could be assigned to vibration of Al–O. The peaks within the range of 1060 to 1165 cm^{-1} were due to the vibration of SO4. Due to the similarities and overlapping peaks between the gypsum and AFm phases, distinguishing them in the system was complex. It is believed that the amount of gypsum in the system was high enough to consume all reactive aluminum phases and still be present in the XRD and FTIR spectra after 360 days for W2. The spectra for W1 and W3 are presented in Appendix A.3.

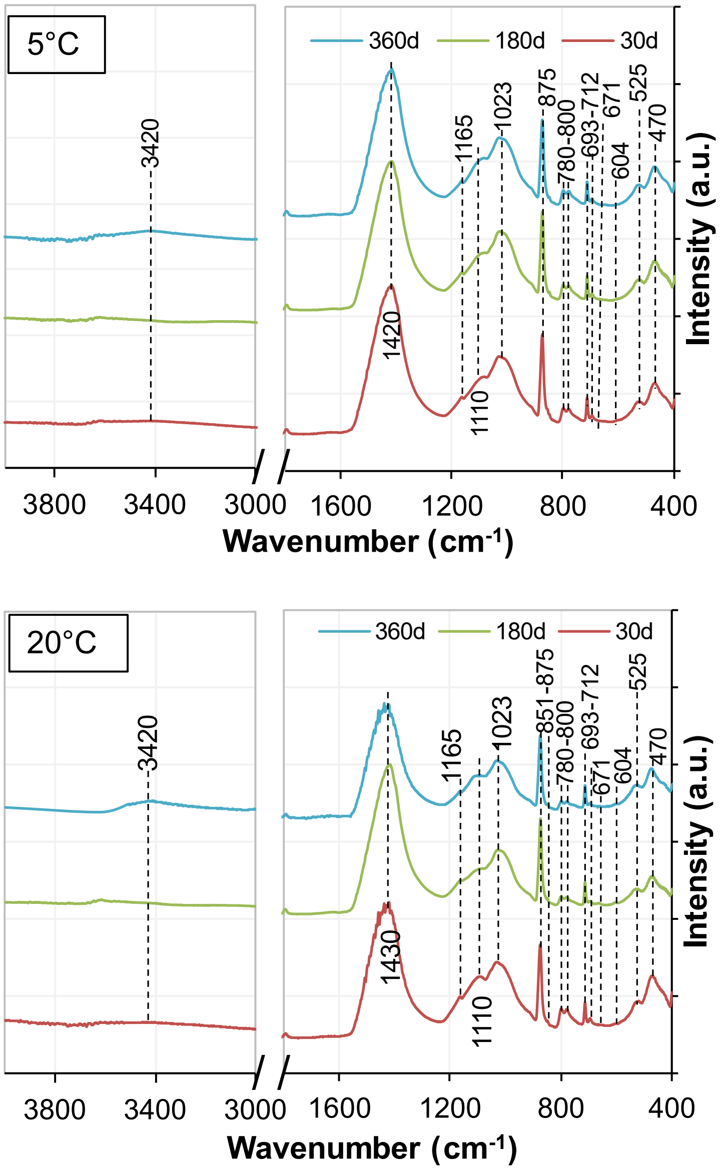


Figure 20. FTIR spectra of Sg + S + FA + W2.

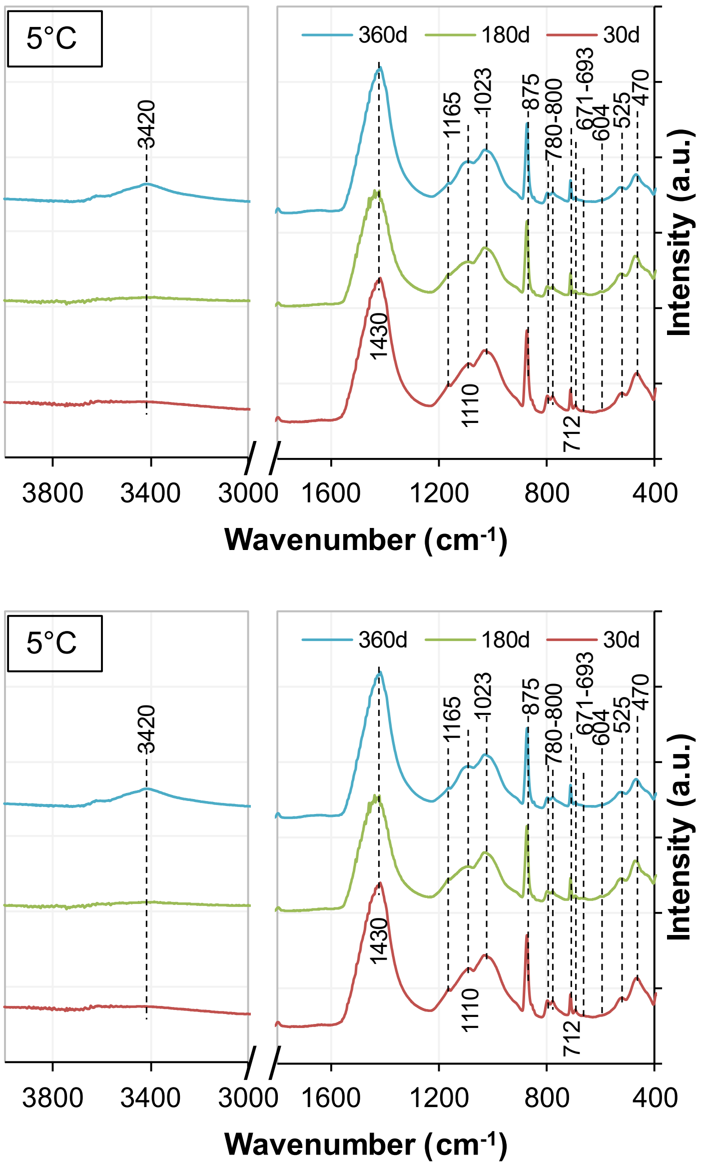


Figure 21. FTIR spectra of Sg + S + C + W2.

Table 6. Interpretation of peak positions observed in FTIR spectra of soil stabilized with WPFA or cement.

Wavenumber (cm^{-1})	Bond	Reference
470	υ_2 Si–O_4^{4-}	450 [38,39], 455 [40], 465 [41]
525	υ_4 Si–O_4^{4-}	525 [40], 521 [42]
604	SO_4	603.72 [13]
671	SO_4	669.3 [13]
693	Si–O	692 [41]
712	υ_4 CO_3	713 [43], 714 [42]

780	Al–O	786 [39]
800	Al–O	814 [39]
851	$\upsilon_3\ CO_3^{2-}$	849 [42]
875	$\upsilon_4\ CO_3^{2-}$	875 [40], 876 [42], 874 [44]
1023	Asymmetric stretching Si–O	950–1100 [41]
1060–1165	$\upsilon_3\ SO_4^{2-}$	1105 [40], 1113 [43], 1116.78 [13], 1116 [22], 1120 [45], 1141.95 [13], 1170 [45]
1420~1430	$\upsilon_2\ CO_3^{2-}$	1425 [13,40], 1458 [42], 1460 [44], 1429 [46], 1422 [22]
3420	$\upsilon_1 + \upsilon_3\ H_2O$	2700–3600 [44], 3433 [46], 3430 [47], 3425 [22], 3450 [38,40], 3444 [43]

To verify these findings, the samples were observed by SEM after 360 days. In both cases, small traces of ettringite could be observed, as shown by red dots in Figure 22.

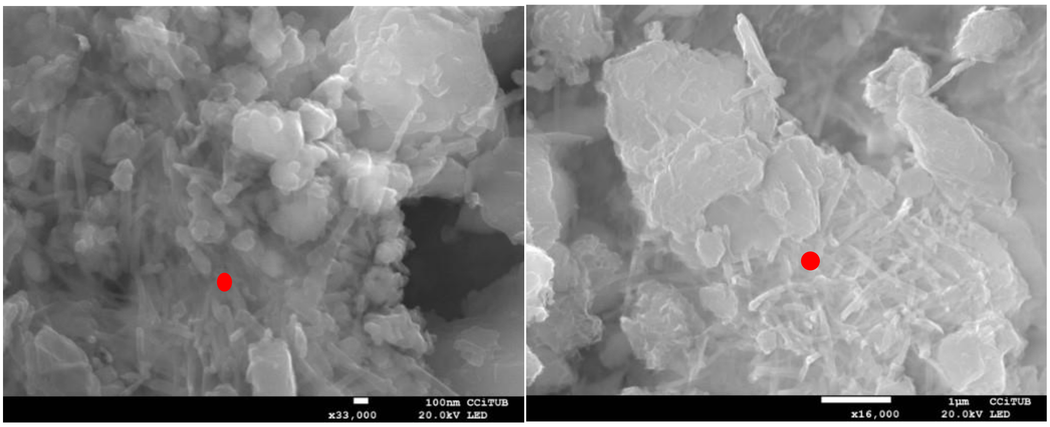


Figure 22. SEM images of soils treated with WPFA (a) and cement (b) at 360 days. Red dots indicate the formation of ettringite.

5.5. Conclusions

A 2-year comparison study was conducted to verify the usability and durability of waste paper fly ash and cement IV as binders in soil samples in different sulfate concentrations. The preliminary results indicated that up to 5% WPFA and 3% cement IV are well suited for a harsh sulfate environment. Acceptable performance is also expected to be obtained with lower sulfate content than proposed in this study. Moreover, future work on determining the feasibility of using WPFA to stabilize different types of soil, with higher sulfate contents should be carried out.

The results of this study revealed the following:

- The unconfined compressive strength (UCS) results after 360 days of WPFA treated soil with different sulfate solutions and different temperatures showed no major changes. The UCS for WPFA after wetting/drying cycles stayed at around 3 MPa for W1 and W3. However, for W2, UCS decreased to about 1.7 MPa, a decrease of 56%, which was expected since only a portion of samples was stabilized with WPFA.
- The UCS of cement samples was significantly reduced compared to those cured at the optimum humidity (90% ± 5% relative humidity) from 6 MPa to 4.3 MPa for both W1 and W3. For samples with W2, the UCS is also decreased by around 2.9 MPa. Although the cement strength was lowered, it was still high enough to surpass the minimum requirement of 2.5 MPa mentioned by Spanish roads and bridges standards.
- The swelling in the samples was tested over 2 years while being exposed to different sulfate solutions and temperatures. The different temperatures and sulfate concentrations had no significant effect on the swelling in soils treated with WPFA or cement. In most cases, a minor shrinkage of around 0.1% was observed. Meanwhile, the weight of the samples increased slightly between 0.02% to 2%.
- Furthermore, the microstructural studies revealed that the formation of ettringite reached its peak after 180 days for samples in contact with subgrade soil. This formation was highest with subgrade soil (W2), intermediate for W3 (20 g/SO_4), and lowest for W1 (tap water). Moreover, after 360 days, the ettringite was partially converted into other poor crystalline AFm phases (e.g., AFm–CO_3, AFm–SO_4, or Friedel's salt), which were not detected due to complexity in the system.

Finally, as shown in this work, extensive laboratory research in the field of waste utilization in civil engineering is necessary for a better understanding of their use and feasibility. This work demonstrated that it is possible to use WPFA as the sole binder for soil stabilization, even in a harsh environment, replacing the commonly used cement.

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Appendix A

Appendix A.1. Swelling Results

The complete swelling figures are presented in this section. Figure A1 represents the swelling/shrinkage in soil stabilized with WPFA and tap water. The maximum weight change belongs to samples at 20 °C which is 1.84%. Additionally, no major swelling/shrinkage was observed in the samples exposed to tap water.

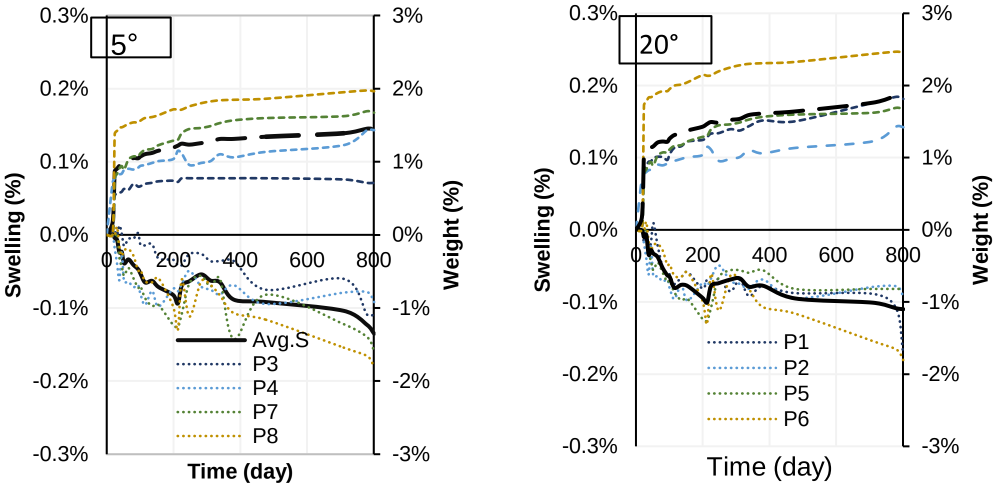

Figure A1. Swelling results in S + F + W1.

Figure A2 shows the swelling/shrinkage in soil stabilized with WPFA and 20 g/L sulfate solution in water (W3). The maximum weight change belongs to samples at 20 °C. The shrinkage in these samples was lower than those exposed with tap water.

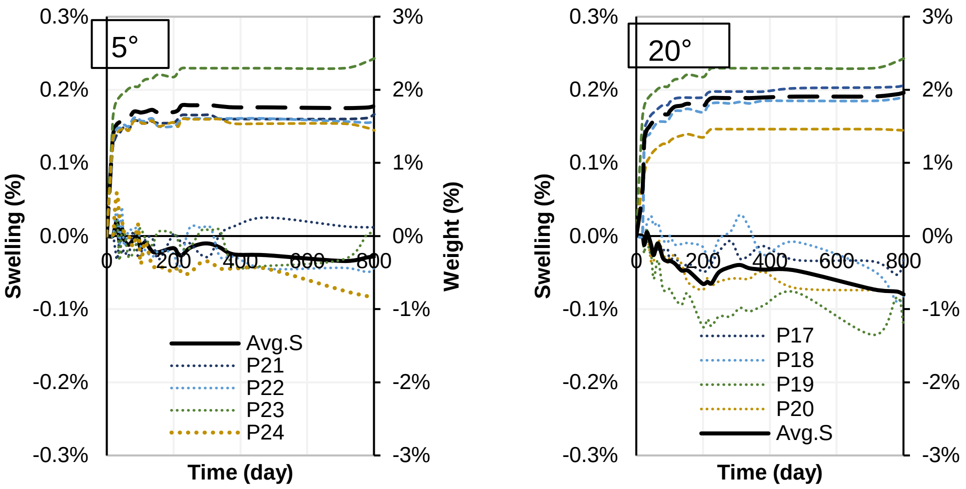

Figure A2. Swelling results in S + F + W3.

The swelling and weight change in soil stabilized with cement and tap water are shown in Figure A3. The weight change in the sample at 20 °C was 1.23%, and the swelling/shrinkage in both temperatures are equal.

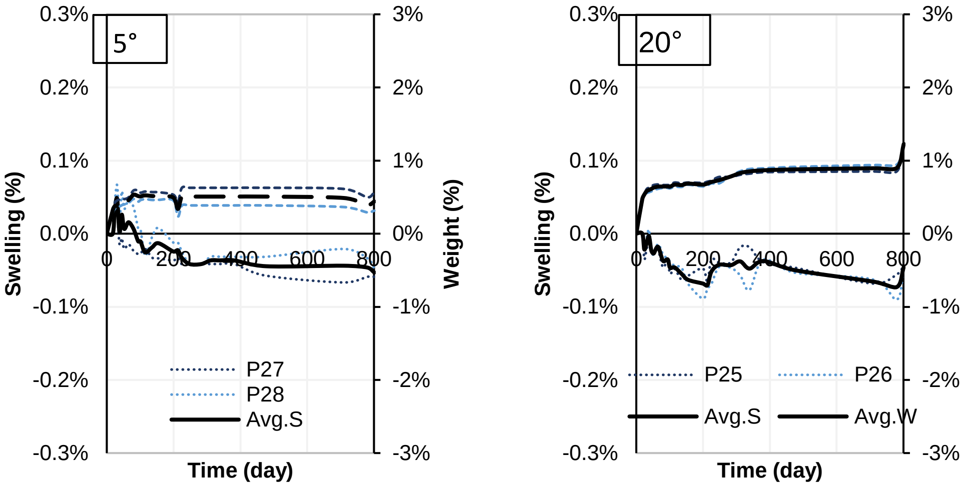

Figure A3. Swelling results in S + C + W1.

Figure A4 presents the soil stabilized with cement and W3. In this also no major changes were observed.

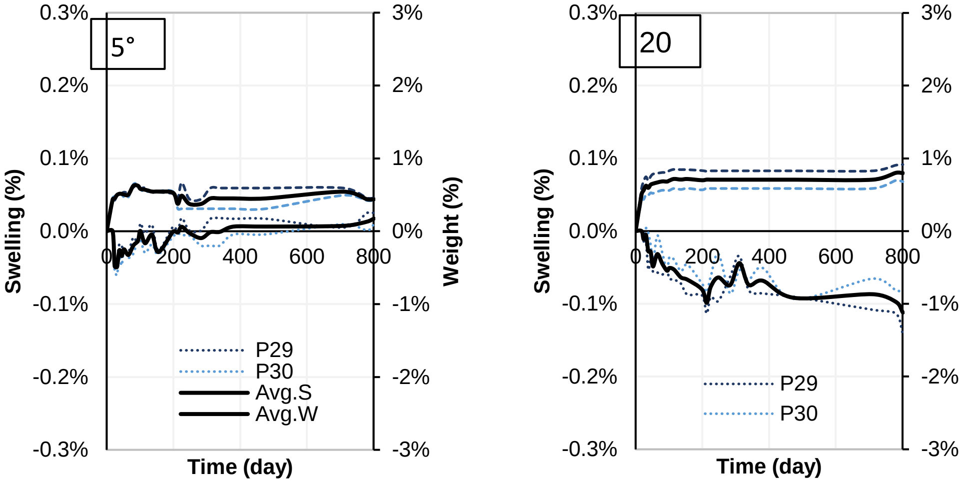

Figure A4. Swelling results in S + C + W3.

Appendix A.2. TGA Results

The complete TGA study are presented in this section. Figure A5 demonstrates the soil stabilized with WPFA and W1. The TGA analysis only showed a peak of calcite. Figures A6–A8 also demonstrated the same results for soil stabilized with WPFA or cement at different temperatures or sulfate concentrations.

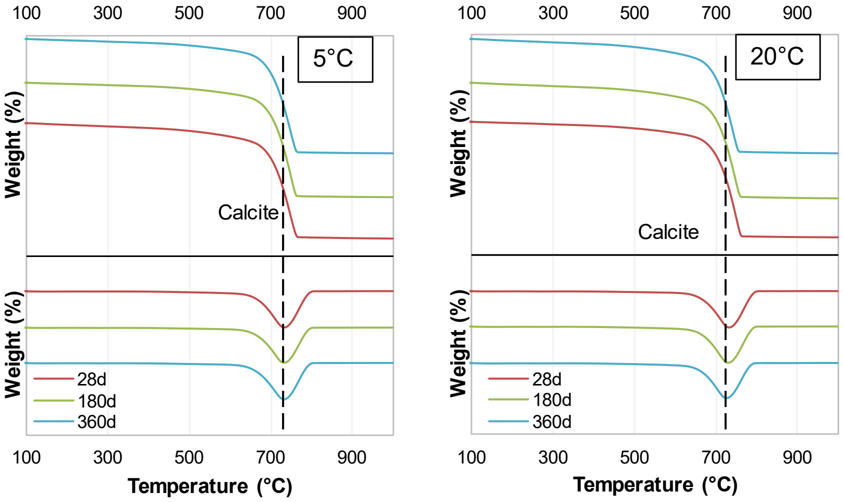

Figure A5. TGA results in S + F + W1.

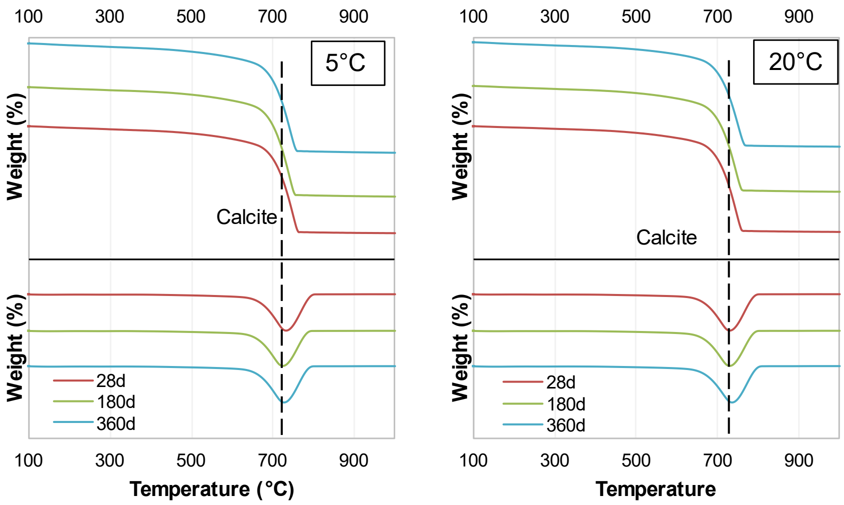

Figure A6. TGA results of S + F + W3.

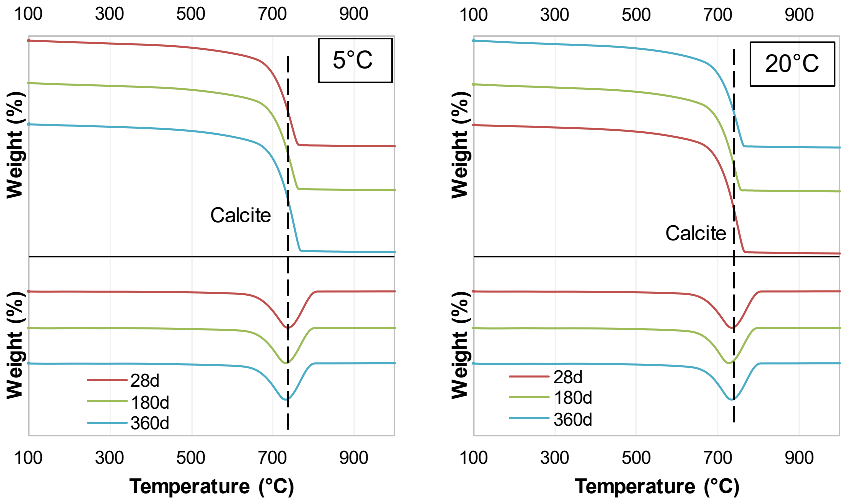

Figure A7. TGA results of S + C + W1.

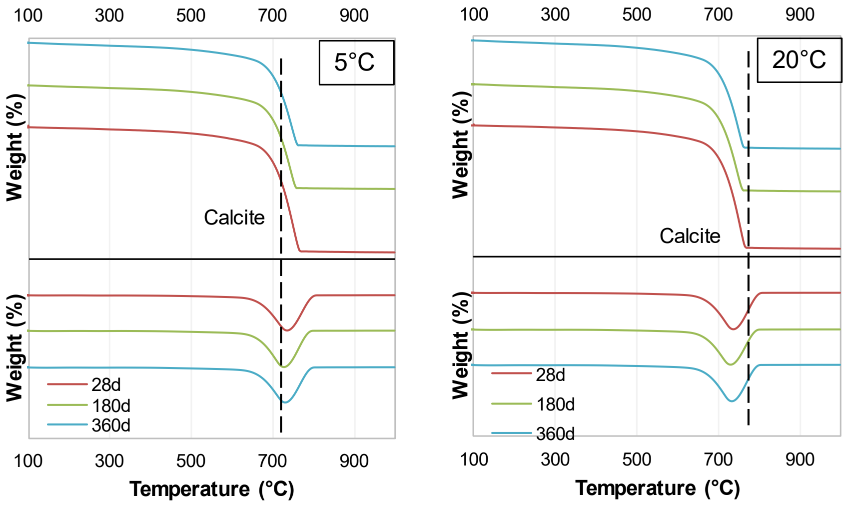

Figure A8. TGA results of S + C + W3.

Appendix A.3. FTIR Results

The FTIR characterization of the soil stabilized with WPFA or cement is described in depth in this appendix. The full FTIR spectra of soil stabilized with WPFA and W1 is shown in Figure A9. The identified peaks are similar to those with W2, with difference of some lower intensities in some cases (normally the SO4 range is lower than those with W2).

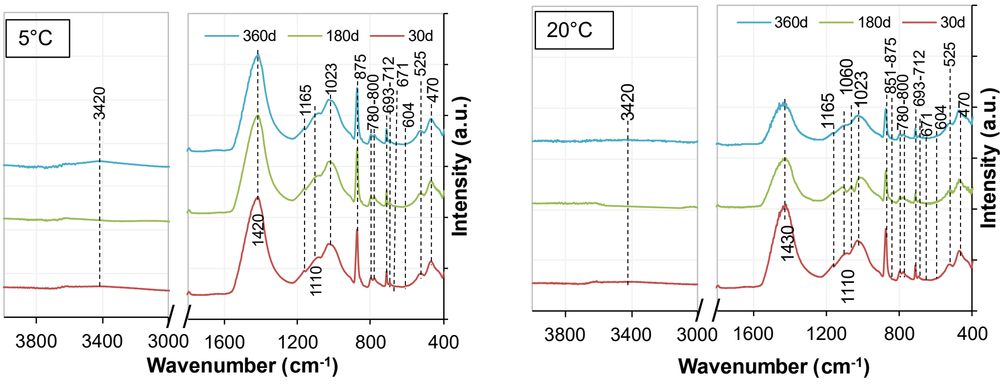

Figure A9. FTIR results of S + F + W1.

The associated SO4 peaks for W3 (Figure A10) are similar to those with W2 and with same intensity except peak at 1430 cm−1. For the cement samples, these peaks are quite similar as identified for Figures A11 and A12.

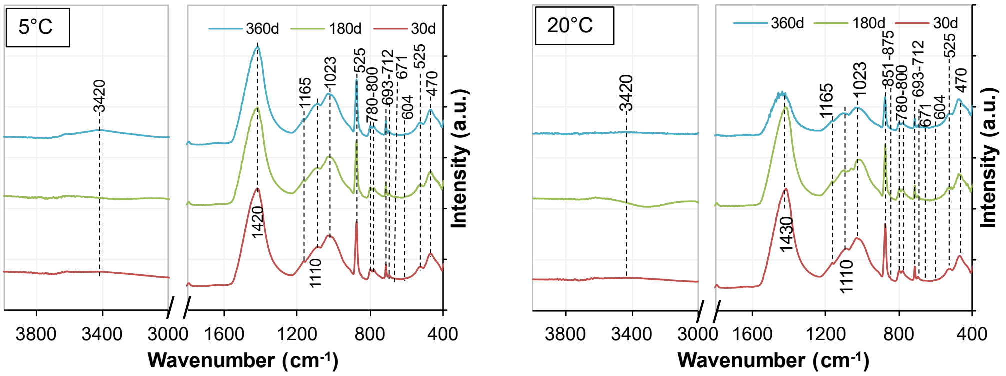

Figure A10. FTIR results of S + F + W3.

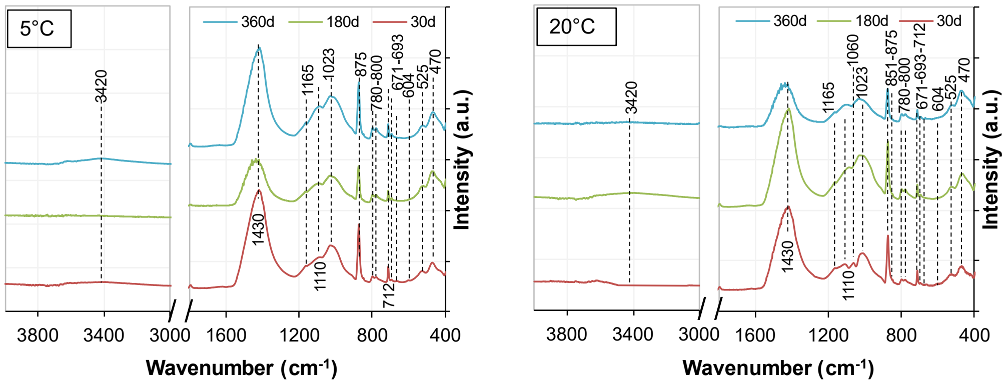

Figure A11. FTIR results of S + C + W1.

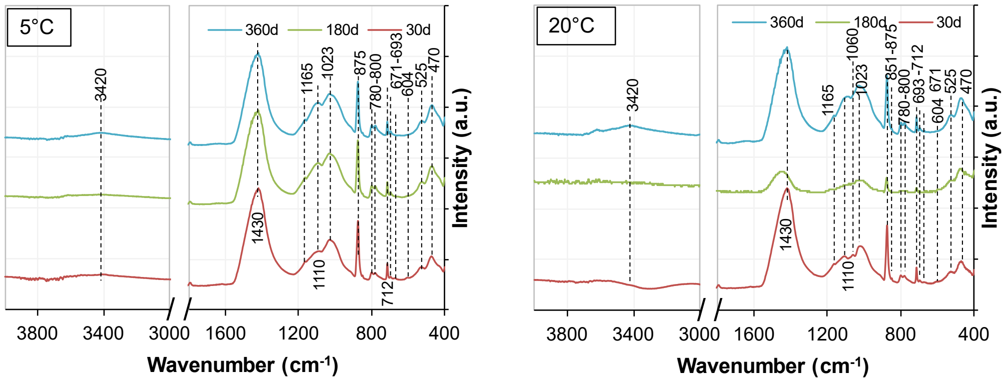

Figure A12. FTIR results of S + C + W3.

Chapter 6

6.1. Alternative Secondary Raw Materials For Road Construction Based On Pulp And Paper Industry Waste

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Book chapter title: Chapter 22. Alternative secondary raw materials for road construction based on pulp and paper industry waste

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Europe represents 25% of the world´s production of pulp and paper, becoming the second largest producer in the world. Waste paper fly ash (WPFA) is a material generated by the incineration of by-products in the manufacture of paper from recycled paper. WPFA has binding properties that allow it to be used as a replacement for cement or lime in soil stabilization. This chapter explains the full-scale application of WPFA in civil works (road projects), from less complex applications to those with high physical-mechanical requirements. The three applications presented here are part of the PaperChain project, funded by the European Union, and are: soil stabilization on a rural road, granular soil stabilization in a local road and, finally, a soil-cement on a regional road. The results obtained show the viability of using WPFA as an alternative binder material to cement or lime.

Keywords: Waste paper fly ash, cementitious material, recycled material, soil stabilization, soil-cement, base and subbase layers, experimental road section and circular economy.

6.2. Introduction

There is extensive research at the laboratory level in the field of the use of waste in civil engineering. However, on the industrial scale, there is much less experience to demonstrate the reliability of the results obtained in the laboratory. This situation often leads to a slow acceptance of the use of alternative materials on an industrial scale. Obviously, a work at industrial level is not a reason for immediate acceptance, very real problems such as the variability of waste composition, the need to implement regulations for the correct use of it, determination of environmental impact, development of treatment plants, etc., should not be left aside.

It should be mentioned that the experimental sections allow a better understanding of the performance of the material studied, as well as the generation of new work methodologies or specific conditions of use, aspects of vital importance for the acceptance of alternative materials.

Today there is a lot of waste that can be incorporated into the construction industry (or civil works). Potential uses have been found for paper processing waste (Frias, 2004; Frias et al., 2008; Ahmad et al., 2013; Ahmadi et al., 2001), steel slag (Ortega-Lopez et al., 2014; Papayianni et al., 2012), fly ash (Indiramma et al., 2020; Zhang et al., 2019; Coudert et al., 2019), water treatment sludge (Tay et al., 2002), gypsum, glass powder (Shen et al., 2007; Bilondi et al., 2018), blast furnace slag (Sharma et al., 2016), limestone grinding dust (Diaz et al., 2020), etc. Many of the materials serve as a partial or total replacement of cement, depending on the final product and its physical, mechanical, durable, and environmental specifications.

The fact that there are alternatives to cement is an excellent advantage since they help to reduce the environmental impact of cement. As is well known, this industry is responsible for between 6% and 7% of CO_2 emissions worldwide (Schneider, 2019). On the other hand, there are applications where the high mechanical performance generated by cement is not totally necessary. In many cases there is a need to generate improvements in civil engineering materials, in the case of soil stabilization, or to develop materials with low-performance levels, in the case of fluid concrete with controlled resistance, where cement content can be totally replaced by other materials, since the strength required is less than 5 MPa.

From this perspective, a waste that has a high potential for use is the ashes from the paper industry. This material has binding properties that can be explored as a material for soil stabilization with different technical specifications. The recovery of this waste will have a great environmental impact since a large amount is taken and deposit into a landfill. Additionally, Europe is facing a change due to the shortage of non-renewable raw materials and the efficient use of existing materials.

The EC initiative "Roadmap to a Resource Efficient Europe", (COM, 2011), aims at a more sustainable use of these resources, turning reject into resources by the reuse of raw materials through 'industrial symbiosis'. From this situation comes the idea of Project Paperchain, which is financed by the European Union through H2020 Programme. The overall objective of PAPERCHAIN is to develop five novel circular economy models centered in the valorization of the reject streams generated by the Pulp and Paper Industry (PPI) as secondary raw material for different sectors: construction sector, mining sector, and chemical industry.

In the case of the construction sector, the objective of the project is to demonstrate the technical performance of the use of waste paper ash (alternative binder) in three cases, from the less complex and easier to reach the market (country roads), to the most complexes and regulated ones (highways).

6.3. Material: Waste paper ash

Europe is the second world producer of pulp and paper, manufacturing 130 million tonnes in 2014 and representing 23% of world production (SDW, 2013). Despite its strategic importance, the activity also has an impact on the environment. This sector is resource-intensive and produces 11 million tonnes of rejects yearly, (BAT, 2015; Nourbakhsh et al., 2009). Reject streams are very diverse in composition and consist of wastewater treatment sludge, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, wood processing residuals, etc.

According to the Confederation of EU Paper Industries (CEPI), PPI reject streams have shown high potential as feedstocks for the production of high-value products in other industries (CEPI, 2014). Nowadays, 55% of the rejects are burned for energy production, land application accounts for 15%, and exploitation of residues in other industries is 10% (EMIR proyect, 2012). 1,65 Mt of rejects generated by the Pulp and Paper industry (15% of the total waste) are still disposed to landfills (Kinuthia, 2016). In addition, the valorization of these rejects also has a direct impact on landfilling itself due to the generation of ashes.

As aforementioned, the paper industry uses large quantities of non-renewable raw materials and has, therefore, increased the use of recycled paper to reduce its environmental impact (Kinuthia, 2016). There are currently plants that use a mixture of both virgin and recycled material for their products, and very few that work directly with recycled paper. During paper production in the latter plants mentioned before, different types of non-hazardous waste are generated, such as pulp rejects, sand, sludge, etc. These wastes have a high energy potential and are therefore used as fuel in energy recovery plants. If this material is used in the generation of energy, at the end of the combustion process, different types of waste are generated, which are mostly ashes. This final product is the material referred to in this chapter.

The conventional process of combustion of paper waste in a recovery plant is carried out in fluidized bed boilers, and the waste is usually pre-treated before entering the boiler. Because the type of paper waste in each plant is different, the plants have many variations. Still, one crucial aspect is the temperature at which the waste is calcined, as it determines the amount of energy generated, such as the quality of the ash obtained.

A general scheme of the boiler system, of an energy recovery plant, is as shown in Figure 22.1. The fluidized bed technology allows a greater use of fuel and also a better transfer of heat produced during combustion. The fluidized bed is formed by the fuel (waste from the paper plant) and the bed itself (ashes, clays, etc.). Combustion takes place at temperatures between 800 °C and 1200 °C (Kinuthia, 2016).

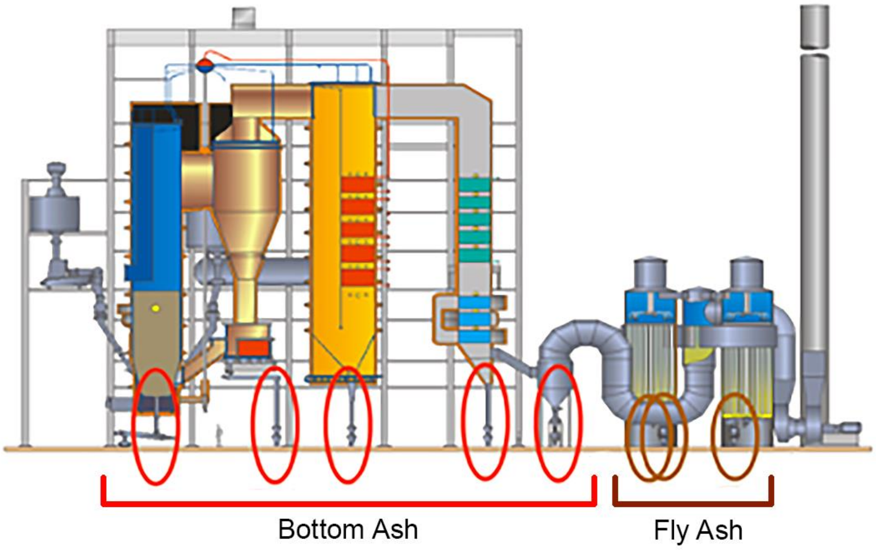

Figure 22.1. Scheme of an energy recovery plant (ERP) and places of collection of the ashes (de la Vega, 2015).

The fluidized bed supports the solid fuel only while air is pumped up during combustion. The result is a cloud that promotes mixing between the fuel and the gas. The coarser particles fall by gravity in the changes of direction of the gas flow. These materials are generally referred to as bottom ash and are classified with LER code 19 01 12 bottom ash and slag (wastes from incineration or pyrolysis of waste). In this type of plant, calcium hydroxide is used to absorb acid gases, as well as activated carbon to absorb dioxins and furans. As the gas flow advances, electrostatic filters or bag filters are used to collect the finer particles. These filters collect what is called fly ash, which is classified under LER code 19 01 14 fly ash (wastes from incineration or pyrolysis of waste) (Decision 93/3/EC).

6.3.1. Waste paper ash characteristics

In this section, only reference will be made to the characteristics of fine ash (waste paper fly ash - WPFA) since these are the ones used in the three cases at the industrial level explained in later sections of this chapter.

The characteristics of the WPFA will depend on the type of waste that enters the boiler and the different materials incorporated into the fluidized bed, as well as those used in the filters. In general terms, this waste is mainly composed of Calcium (49%), Silica (12%), and Aluminium (12%). Other compounds are also found, but in very low quantities, such as Magnesium (1.5%), Titanium (1.4%), and Sulphur (1.0%) (Table 22.1). The WPFA presents a loss by calcination (LOI) of approximately 17%, as shown in Figure 22.2.

Table 22.1. Chemical composition of different samples of WPFA.

Element (wt. %)	CaO	SiO_2	Al_2O_3	MgO	TiO_2	SO_3	Fe_2O_3	P_2O_5	Other
S1	48.86	12.40	12.42	1.71	1.00	0.71	0.83	1.03	1.88
S2	49.43	11.73	11.65	1.62	0.97	0.59	0.84	0.08	2.23
S3	49.55	11.04	13.72	1.51	0.99	0.61	0.82	0.64	1.30
S4	47.64	12.36	11.90	1.61	1.41	1.05	0.95	0.83	2.44
S5	49.04	13.00	10.94	1.75	1.27	1.19	1.04	0.87	2.40
S6	48.13	12.76	12.91	1.66	1.32	1.05	1.00	0.92	2.55
S7	48.30	12.43	12.09	1.59	1.21	0.95	0.93	0.83	2.21
S8	49.36	12.20	9.99	1.62	1.36	1.05	0.99	0.74	2.24
S9	48.33	10.99	11.48	1.43	1.24	0.91	0.97	0.56	2.23
S10	48.90	12.37	11.19	1.79	1.44	1.16	1.05	0.96	2.55
S11	50.39	10.49	11.08	1.45	1.12	0.85	0.80	0.56	1.99

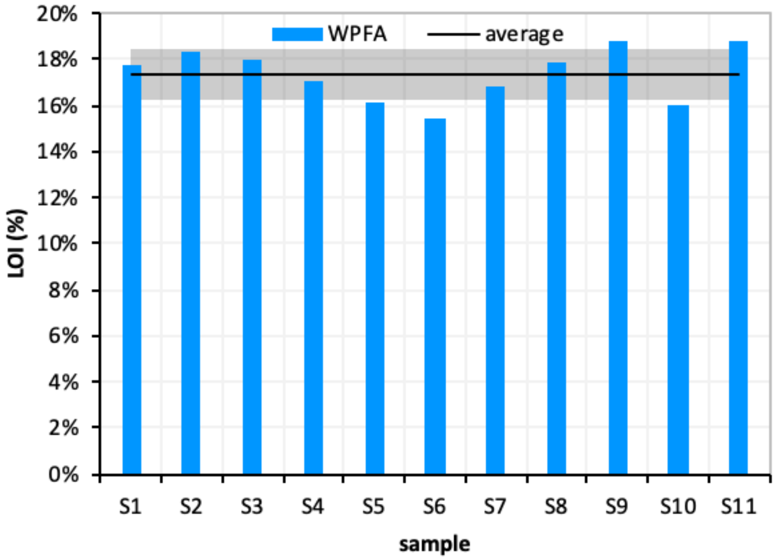

Figure 22.2. Variation of LOI of different samples of WPFA.

The mineralogical composition of ash will depend, as well as the chemical composition, on the raw materials, but it will also be affected by the combustion temperature in the fluid bed and the cooling speed of ash. As shown in Figure 22.3, the diffraction spectra show a fairly crystalline material with a low amorphous fraction. Within the crystalline phases are Calcite ($CaCO_3$), Lime (CaO), Portlandite ($Ca(OH)_2$), Quartz (SiO_2), Calcium silicate (Ca_2SiO_4), Gehlenite ($Ca_2Al_2SiO_7$), Aluminium (Al), Halite ($NaCl$), and Mayenite ($Ca1_2Al1_4O_{33}$). The mineralogical composition determined in these ashes is similar to those reported in other investigations (Frias et al., 2008; Mozaffari et al., 2009). The presence of lime can have a negative effect as hydration produces an expansion, which must be taken into account when using it, and make a previous slaking as shown in the work of Baloochi et al. (2019).

It is important to highlight lime's existence that, in the presence of water, will react to form portlandite. And together with the existing one, with time will carbonate generating slow-reacting agglomerating compounds. It is also important to note the presence of calcium silicates, as these in the presence of water can hydrate and provide hydraulic properties to the ash. The compounds present in the ashes show potential for hardening and develop strength, which can be similar to that of an aerial or hydraulic lime, but less than Portland cement (Kinuthia et al., 2001).

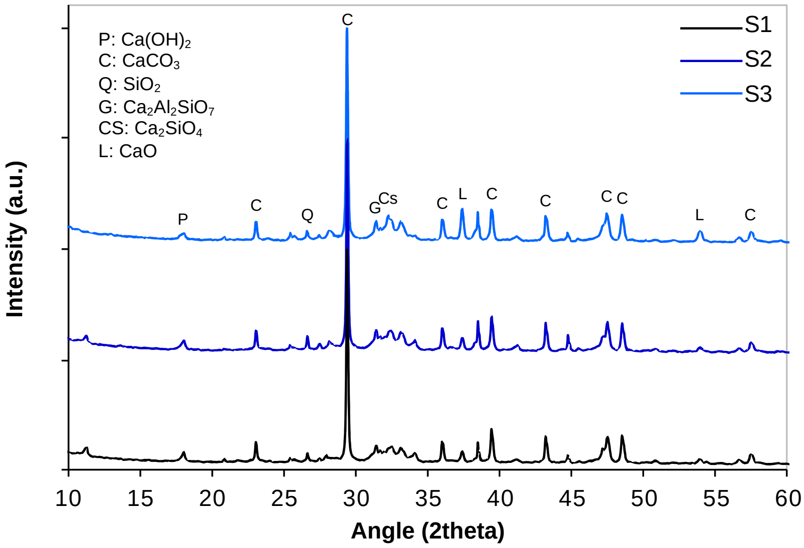

Figure 22.3. XRD patterns of different samples of WPFA.

The finesses of WPFA is high because they are collected in the electrostatic filters or the bag filters, and are the particles remaining in the gas flow. As shown in Figure 22.4, the average size of this ash is 10 microns and contains particles in the range of 0.05 - 100 microns, which can be found in some types of Portland cement. It can also be seen that the size variation of the different samples is not significant. Having a small particle size is of great help in the hydration or carbonation reactions of the material.

The study of the WPFA using scanning electron microscope allows to observe that these are irregular particles with high specific surface area (quite small particle sizes) (Figure 22.5 and Figure 22.6.) The high specific surface area and the porosity of the particles should be taken into account when using the WPFA as they can generate some handling problems, as mentioned by Segui et al. (2013).

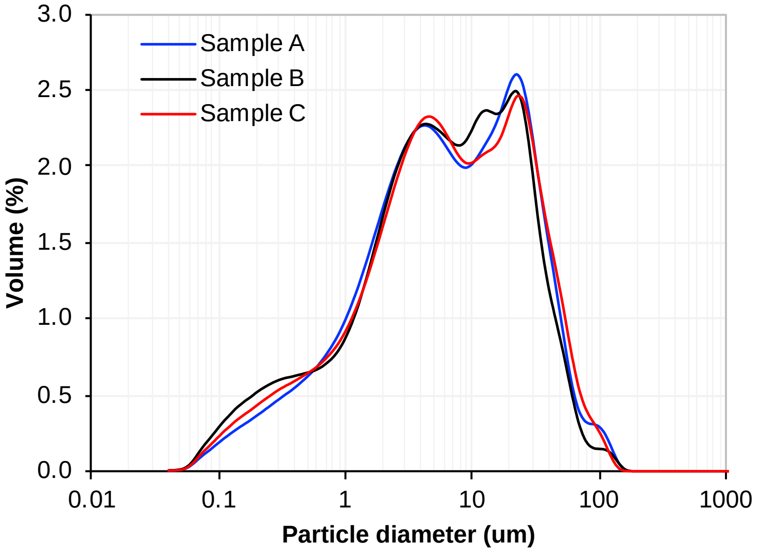

Figure 22.4. Variation of size distribution of different samples of WPFA.

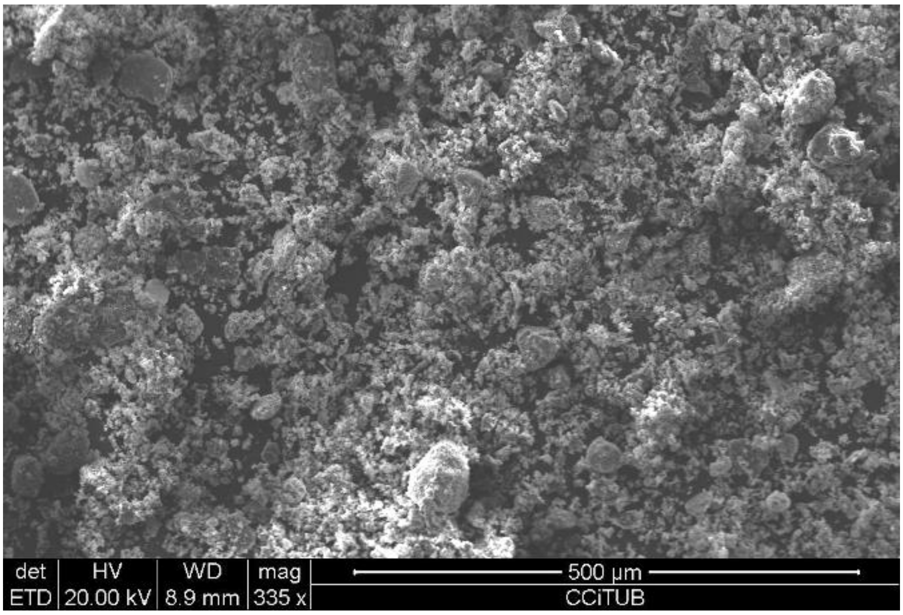

Figure 22.5. General view of a typical WPFA sample.

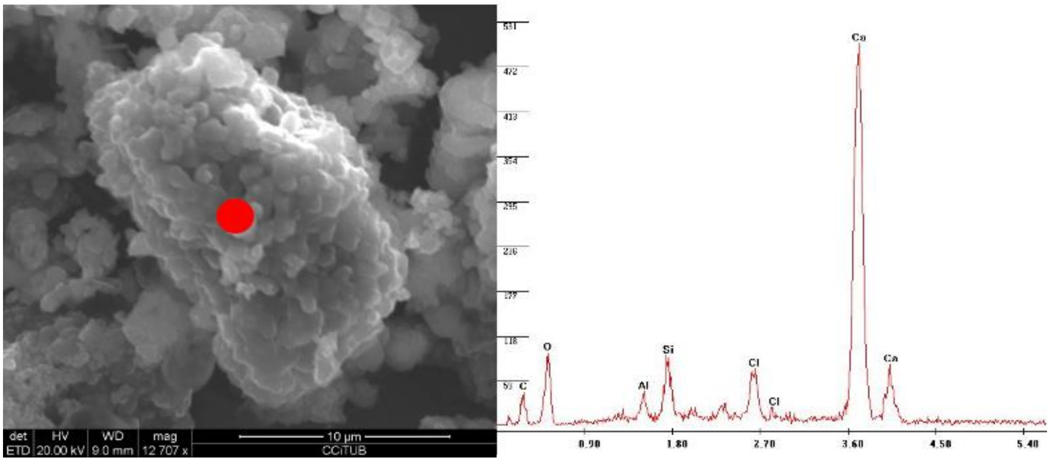

Figure 22.6. Micro-analysis of an ash particle, in which the presence of calcium, silica, aluminium and chlorine is determined.

The WPFA density is in the range of 2.60 to 2.70 g/cm^3, which is less than an added cement, that can be in the range of 3.0 g/cm^3 and has a pH value above 12.

6.4. Soil stabilization with cementitious materials

Due to mechanical and environmental requirements, transport infrastructure works need to increase the physical, mechanical, and durability properties of soils, where quality requirements are higher due to traffic loads. However, soils do not always meet these requirements.

Soils that do not meet the requirements for use in infrastructure can be improved by using different products to enhance their performance, reduce sensitivity to water, increase their bearing capacity, or improve their resistance to deformation. The most commonly used products are Portland cement, with additions, and aerial limes. The latter can be used in powder or slurry form. Both cement and lime are mixed with the soil, which can be in plant or in-situ, spread, compacted, and cured.

Portland cement is usually used with granular or fine soils, which, when hydrated, produce bonds among the soil particles, significantly increasing the deformation resistance of the stabilized soil. limes are generally used with fine or clay soils, reducing their plasticity, as well as reducing their swelling. The reaction is by ionic exchange with the compounds in the soil, resulting in a pozzolanic reaction with a slow development of properties.

Depending on project requirements, stabilized soils of different categories may be required. Stabilization is intended to generate an increase in the soil's bearing capacity, an increase in its resistance to deformation under load (Figure 22.7), and a decrease in water sensitivity. If there is a high amount of granular fraction in the soil, the amount of binder will be low, and good properties of the stabilized soil will be obtained. The structural contribution of an improved or stabilized layer as a base for pavement is very important, and because of this, its use in road infrastructure is necessary.

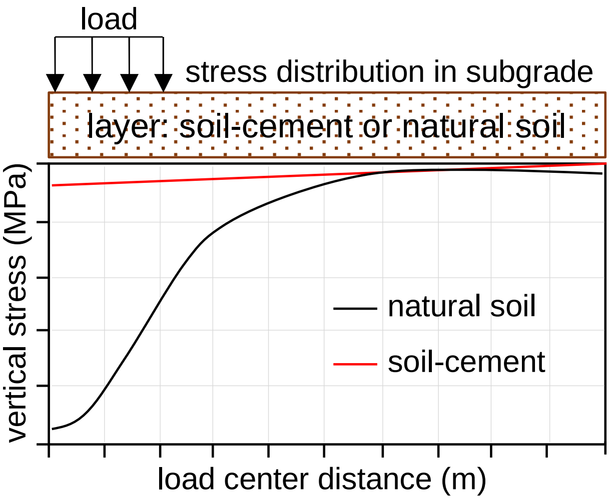

Figure 22.7. Differences between the stresses distributed to the subgrade by granular and cement-treated layers (adapted from (Manual of cement-treated layers, 2005)).

The pavement is a set of superimposed layers relatively horizontal made of different materials, properly compacted, that are placed on the subgrade (Figure 22.8). The subgrade is the foundation of the pavement and must also be prepared to act as a resistant and durable platform (Manual of cement-treated layers, 2005). The functions of the pavement are to provide a safe and comfort surface with permanent characteristics under repeated traffic during the service life, to resist and distribute traffic loads and to protect the subgrade from the weather conditions.

Depending on the materials composing the layers, there can different types of pavements: flexible, semi-rigid and rigid pavements.

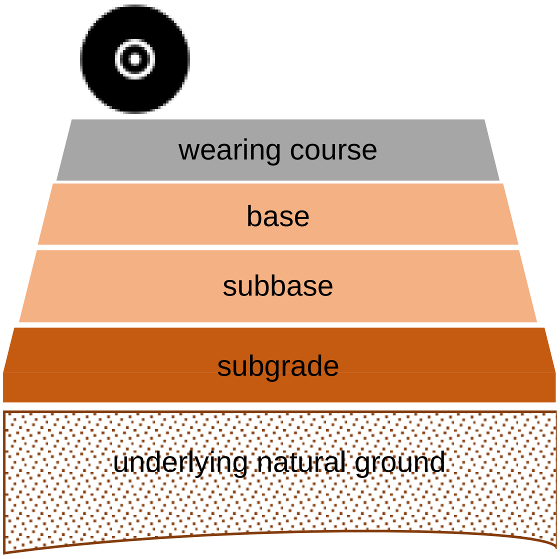

Figure 22.8. Pavement structure.

Flexible pavements are composed of asphalt layers in the wearing and binder courses laid over a bases and subbases. Bases can be granular or asphalt layers and subbases are exclusively granular. Semi-rigid pavements are also composed by asphalt layers placed over cement treated layers (bases and subbases), and rigid pavements are made of Portland cement concrete placed on different types of bases and subbases (they can be granular, cement-treated and lean concrete layers).

In all cases the wearing course must bear traffic stresses and provide functional characteristics. In the case of flexible and semi-rigid pavements, bases absorb most of the vertical stresses and subbases provide a uniform foundation to the base and a suitable working platform. In the case of rigid pavements, due the high stiffness of the cement concrete which distributes the vertical loads over larger areas, the stresses transmitted to bases and subbases are very low (Manual of soil stabilization with cement or lime, 2004; Kraemer et al., 2009).

Empirical or analytical methods can be used to design or dimension the pavement, although it is also common to find methods that combine both of them. Regardless of the method used, dimensioning requires the definition of different factors:

- Life-span for which the pavement is designed;
- Traffic that will be supported by the pavement (intensity and composition of the traffic, load distribution);
- Load-bearing capacity of subgrade;
- Characteristics of the materials that make up the different layers of the pavement;
- Climatic conditions that affect the behavior of the pavement (temperature, rain, etc.).

In Spain, pavement design is carried out by means of catalogs, whose preparation has taken into account analytical models and empirical considerations, using Standard 6.1 IC (pavement sections - road instructions) (2003), together with PG-3 (General Technical Specifications for Road and Bridge Works) (2014).

The standards mentioned above present a range of structural pavement sections, made up of materials with standardized characteristics, defined according to the support capacity of the subgrade and the heavy vehicle traffic that the road can support. For each combination of traffic category and subgrade type, several possible pavement sections are defined.

6.5. Case studies on the use of waste paper ash in road pavement construction

The case studies shown in this chapter have been developed within the PaperChain project, which aims to demonstrate in the construction sector the use of WPFA as an alternative cementing material to replace lime or cement in soil stabilization work on road projects. In all cases, ACCIONA has been responsible for the design and execution of the stretches. The ashes have been supplied by SAICA (Spanish Pulp and Paper Industry), and UPC (Universitat Polìtecnica de Catalunya) has provided the technical support for initial tests, durability tests, and monitoring. Finally, TECNALIA has carried out environmental monitoring.

The pilots have been built in real conditions and use, following standard construction practices and using the same equipment and machinery as for regular soil stabilization works. By this strategy, the impact of the new product on productivity can be measured and improved. Also, the builders can evaluate in a better way the advantages and disadvantages of the proposed application.

In Spain, PG-3 (General Technical Specifications for Roadworks and Bridges) is the reference code in the road construction sector. The characteristics of stabilized layers are detailed in the following articles:

- Article 512: “In situ stabilized soils”.

- Article 513: “Cement-treated materials (cement-stabilized soil and cement-bound graded aggregate)”.

The cited articles described four potential stabilized soil layers depending on the technical requirements, position within the road section, and type of starting soil to be stabilized (Table 22.2).

Table 22.2. Relationship between the different stabilized layers, location and requirements.

S-EST1	In situ stabilized soil type 1	Stabilized soil for subgrade formation	↓ Increased mechanical requirement
S-EST2	In situ stabilized soil type 2		
S-EST3	In situ stabilized soil type 3		
SC	Soil-Cement	Road subbase material	

Stabilized layers S-EST1 and S-EST2 correspond with the subgrade formation. Normally they correspond with natural soils that are stabilized to improve their bearing capacity and/or to reduce swelling or potential collapse. These soils are usually clay or clayey silts and can be treated with hydrated lime or cement depending on their plasticity.

Typically, this layer, S-EST1 or S-EST2, can form the embankment foundation and sometimes the core, too, if there is no better material available. The main requirement is CBR (must be higher than 6 for S-EST1 and 12 for S-EST2 type). Swell or collapse must be eliminated.

High heavy traffic roads normally contain additional stabilized layers on the embankment crown (subgrade), like a capping layer. This is the S-EST3 stabilized layer. Sometimes, the overlying layer (the subbase) can be stabilized too, and receives the name of Soil-cement layer. The different pilot sections are shown schematically in Figure 22.9.

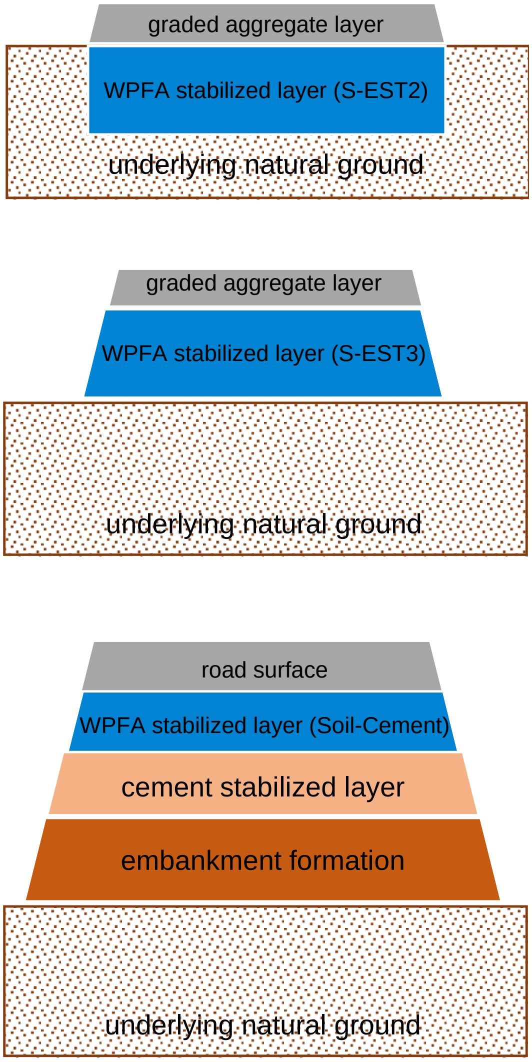

Figure 22.9. Diagram of the different stabilized layers within the road section.

Some of the technical requirements for the different layers of stabilized material and the related Spanish standards are shown in Table 22.3.

6.5.1. Stabilized layer S-EST2 type according to the Spanish road regulation

The one km long unpaved road pilot for layer S-EST2 is located in Ejea de Los Caballeros, Spain, and was built in October 2018 (Figure 22.10). The town of Ejea de Los Caballeros, mostly dedicated to the intensive agriculture industry, has a network of unpaved rural roads that hold heavy traffic. However, the area where the road pilot was built is mostly used for recreation and has low traffic with a minimum contribution of heavy traffic. An exception happened in January 2020, when due to works on the main roads, a heavy load of traffic was diverted this way.

The objective of this pilot was to demonstrate the technical and economic feasibility of using WPFA as a cementing agent and total lime replacement in soil stabilization

Table 22.3. Stabilized and soil-cement technical requirements according to PG-3 (2014).

Characteristic	**Unit**	**Standard**	**Material type**			
			S-EST1	**S-EST2**	**S-EST3**	**SC**
Binder content	% by mass of dry soil	---	≥ 2	≥ 3		
CBR at 7 days	CBR	UNE 103502	≥ 6	≥ 12	n/a	
Compressive strength at 7 days	MPa	UNE EN 13286-41	n/a		≥ 1.5	≥ 2.5 ≤ 4.5
Density (modified Proctor test)	% of Maximum Dry Density	UNE 103501	≥ 95	≥ 97	≥ 98	
Particle size distribution (soil/aggregate)	---	UNE EN 933-1	UNE 103101			Size grading interval depending on the traffic.
Soluble sulphate content (original soil)	% by mass of dry soil	UNE 103201	SO_3 < 0.7%			SO_3 > 0.5% employ sulphate resistant cement
Organic matter content (original soil)	---	UNE 103204	< 2	< 1		≤ 1
Plasticity index (treated soil)	---	UNE 103103 and 103104	---			Liquid limit < 30 and Plasticity Index < 12
Free swelling test	%	UNE 103601	0 at 7 days.			n/a
Layer thickness	cm	---	≥ 25 ≤ 30			≥ 20 ≤ 30
Stabilized soil moisture compaction	% by mass of dry mix	UNE 103300	± 2% of modified Proctor test			-1% / +0.5%
Load test (Plate)	MPa (14 to 28 days age)	UNE 103808	$Ev_2 \geq 60$ $Ev_2/Ev_1 < 2.2$	$Ev_2 \geq 120$ $Ev_2/Ev_1 < 2.2$	$Ev_2 \geq 300$ $Ev_2/Ev_1 < 2.2$	n/a

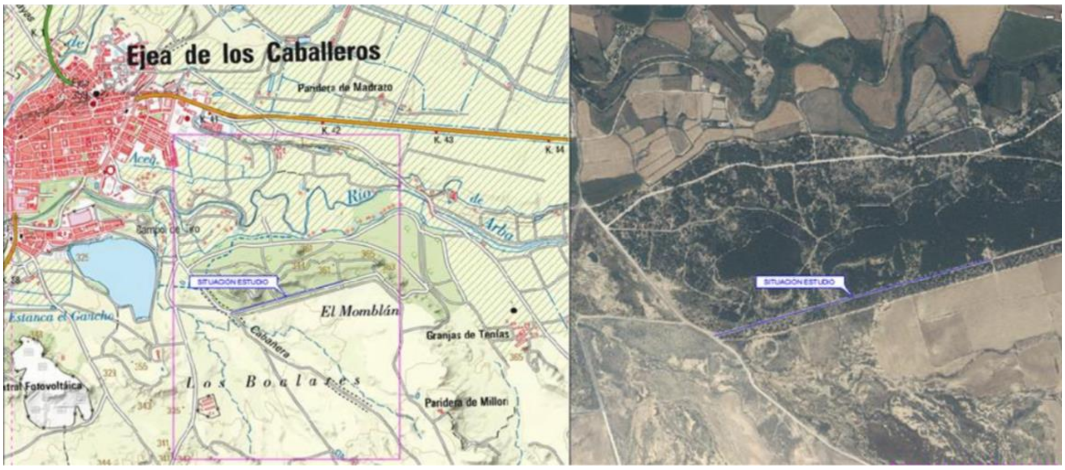

Figure 22.10. Field trial location (S-EST2).

The original unpaved road was made of 10 cm graded gravel located over a clayey surface called "buro" by locals. This type of clay is not apt for agriculture as it is not arable for being high in salt and presenting poor drainage properties (Figure 22.11). In rainy seasons, heavy trucks are diverted into unpaved roads, causing costly damages in the clayey areas, which are most susceptible to water.

Figure 22.11. Original surface (left) and surface after gravel removing (right).

The stabilized-soil used for this pilot was the S-EST2 type, as defined by the Spanish standards. In the past, this road was repaired, adding a thin layer of gravel, so that layer was removed to treat just the clayey soil. Along one km of road, the soil was characterized to define the working formula using WPFA. In the initial tests, 2%, 3%, and 4% of WPFA are used to stabilize the soil and reach the CBR value specified in the standard (CBR ≥ 12). All compositions reached the necessary CBR value but, to ensure a more reliable scenario, 3% WPFA content was set.

The final design was conducted with a 25 cm thick WPFA soil-stabilized layer and included a replacement of 10 cm-thick graded aggregates on the surface (Figure 22.12).

Figure 22.12. Soil stabilization process: 3% WPFA dosing and mixing, levelling and compacting.

The quality control tests were executed in the laboratory using samples of blended material taken from the pilot road. The bearing capacity was tested using a plate load test on the resulting layer. All quality control tests fulfilled the requirements according to the standards for this type of stabilized soil (Table 22.4). Last, the pilot road was covered with 10 cm of graded aggregate.

6.5.2. Stabilized layer S-EST3 type according to the Spanish road regulation

The Pilot 2 for layer S-EST3 took place in the small village of Villamayor de Gállego, located near Zaragoza, Spain. It consisted of a 300 m long stretch on a local paved road and another 700 m on a rural unpaved road. Both stretches underwent heavy traffic due to the vicinity of an agricultural cooperative, and travelers would also use this road to avoid crossing through the nearby city center. However, there is no official data for the Annual Average Daily Traffic on this particular road. In detail, the experimental trial corresponds with Balsa Street (Figure 22.13).

Table 22.4. Quality control test of WPFA-stabilized soil S-EST2 type.

Test	**Original soil**	**Requirement**	**WPFA-stabilized soil**
Soaked CBR at 7 days	at 95% MDD: 4.2	at 97% MMD ≥ 12	at 95% MDD: 30
	at 98% MDD: 5.6		at 98% MDD: 47
	at 100% MDD: 6.7		at 100% MDD: 70
Plate load test	N/A	Ev_2 > 60 MPa for subgrade E1	Ev_2 > 224 MPa Improved subgrade E2
		Ev_2 > 120 MPa for subgrade E2	
		Ev_2 > 300 MPa for subgrade E3	

Figure 22.13. Field trial location (S-EST3).

After being characterized (Table 22.5), the soil of the borrow pit was treated with different replacements of WPFA to fulfill the S-EST3 layer requirements, according to PG-3 (Table 22.6). The main goal of this pilot was to meet these requirements using WPFA instead of cement.

Table 22.5. PG-3 requirements for stabilized soil in-situ (S-EST3) and Villamayor soil.

Characteristic	**Unit**	**S-EST3 layer**	**Villamayor soil**
Compressive strength at 7 days	MPa	≥ 1.5	---
Density (Modified Proctor)	% of MDD	≥ 98	---
Organic matter	% mass	< 1	0.08
Soluble sulphate	% mass	< 0.7	0.04
Atterberg limits	---	Liquid limit (LL) ≤ 40 Plasticity index ≤ 15	Non plastic
Particle size	% pass through sieve	80 mm = 100% 2 mm > 20% 0.063 mm < 35%	80 mm = 100% 2mm = 32% 0.063 mm = 9%

Table 22.6. WPFA quantity tested to meet PG3 requirements.

Composition	**Compressive strength at 7 days and 98% of MDD**
Soil + 3% Cement type IV (reference)	5.2 MPa
Soil + 3% WPFA	1.6 MPa
Soil + 5% WPFA	2.9 MPa
Soil + 7% WPFA	3.3 MPa
Soil + 9% WPFA	4.7 MPa

At the laboratory scale, 3% of WPFA fulfilled the strength requirement but, due to not accurate dosing at the employment of heavy machinery, the selected dose rate was 5% of WPFA. With that amount of waste paper fly ash, the optimum moisture of the mix was 8.2%, according to the compaction tests.

During the design works, the agricultural machinery traffic was taken into account, so it included additional covering treatment. The standard solution is a double bituminous surface dressing, that consists of an emulsion application covered with 4-8mm aggregate and rolled with tyred pneumatic, followed by a second emulsion application covered with 2-6mm aggregate, and rolled again.

The materials in the stretch were heterogeneous. Therefore, it was necessary to take 10 cm off the surface layer before hauling the pit soil to simulate the leveling and compaction suitable for S-EST3 stabilization.

The test previously conducted at the laboratory indicated that, besides using a fly ash content of 5% and water content of 8.2%, there was to be a delay of 30 minutes following the mix of WPFA, soil, and water. It should also be compacted with less moisture than optimum until achieving the highest dry density under the Modified Proctor Test.

Upon completion of the leveling, the WPFA-soil mix spread out using a dry process (Figure 22.14), a protective surface layer was created using laying out the emulsion-gravel treatment (Figure 22.15). The process is similar to the S-EST 2, with the only difference being the content of WPFA and moisture.

The resulting materials were sampled and tested for compressive strength at the laboratory and afterward tested for its bearing capacity on-site. The results obtained are shown in Table 22.7.

Figure 22.14. Soil stabilization process: 5% WPFA dosing dry process, machinery and mixing (S-EST3).

Figure 22.15. Bituminous surface dressing(S-EST3).

Table 22.7. Quality control test of WPFA-stabilized soil S-EST3 type.

Test	Original soil	Requirement	WPFA-stabilized soil
Unconfined compressive strength at 7 days	n/a	at 98% MDD ≥ 1.5MPa	at 98% MDD: 1.8MPa
Plate load test at 14 days (30 cm diameter)	n/a	Ev_2 > 60 MPa for subgrade E1 Ev_2 > 120 MPa for subgrade E2 Ev_2 > 300 MPa for subgrade E3	Ev_2 > 334 MPa Improved subgrade E3

6.5.3. Soil-cement layer type according to the Spanish road regulation

The soil-cement layer pilot was located on the highway connection between the A31 and A33 roads in Spain, linking the northern and southern Mediterranean coasts. This stretch is also known as the "La Font de la Figuera" bypass, and it is an ACCIONA's construction project (Figure 22.16). The pavement section is type 232 of Standard 6.1 IC of the Spanish Highway Instruction. The section is composed of of 15 cm of bituminous mixtures over 20 cm of soil-cement over an E3 formation level (Ev2 > 300MPa Standard UNE 103808). All the cement on this layer of soil-cement was replaced with WPFA. The rest of the highway had regular soil-cement and was used to study the compared performance of both stretches.

Figure 22.16. Field trial location (soil-cement).

The granular material used came from the Cantalar Quarry, the same used by the construction site on the soil-cement layers. Two different sets of samples for laboratory testing, 0-32 mm and 0-6 mm, were taken. The mix to be tested consisted of 90% of the fraction 0-32 mm mixed with 10% of the fraction 0-6mm. The aggregate mix fulfills the requirements of Article 513 of PG-3 Materials treated with cement (soil-cement and gravel-cement). The organic matter is below 1%, and it fits in the SC40 grading envelope, the soluble sulfates (SO3) are less than 0.5%, and it has a Plasticity Index lower than 12 (as a non-plastic material).

Once the granular mix material was considered suitable, the soil-cement composition was defined with the content of binder and moisture capable of reaching 98% of its maximum dry density (Modified Proctor), and unconfined compressive strength between 2.5 and 4.5 MPa at 7 days. In the case of the use of WPFA, a series of remolded specimens were manufactured, varying the ash and moisture content until the formula was optimized. In the case of using cement, the PG-3 defines the minimum content at 3%, which was also tested in order to confirm the target is met. Table 22.8 shows the test performed to obtain the optimal composition.

Table 22.8. Test results to obtain the optimal composition. Soil-cement.

Material	**Maximum density and optimum water content**	**Compressive strength at 7 days**

Soil Not treated	2.241 t/m^3 5.9%	---
3% CEM IV/B 32.5	2.242 t/m^3 6.3%	3.5 MPa
4% WPFA	2.172 t/m^3 7.6%	2.5 MPa
6% WPFA	2.156 t/m^3 7.4%	3.7 MPa
8% WPFA	2.103 t/m^3 7.1%	4.3 MPa

Because of the uncertainty with this alternative soil-cement and possible humidity and binder content variations in the worksite, the objective strength was increased 20% at the laboratory level (3 MPa instead of the 2.5 MPa at 7 days). Attention was also paid to achieving a material stiffness similar to the standard SC adjacent to the test section (3.15 MPa at 7 days). Taking into account these conditioning factors, the optimal composition was achieved with the following parameters:

- WPFA dose = 5% w/w of aggregate.
- Optimum water content = 7.5%.
- Maximum dry density = 2,164 t/m3 (98% MDD = 2,121 t/m^3).
- Unconfined compressive strength at 7 days = 3.23 MPa.

In the mixing plant, a silo was loaded with WPFA, and mix design tests were carried out to adjust the necessary quantities (Figure 22.17). Relevant adjustments were made in the plant to achieve the material with the required content since WPFA has a lower bulk density than cement and a greater content. In total, 105 tonnes of fly ash were employed in the trial.

Figure 22.17. Soil-cement plant.

After placing and compacting the soil-cement, this layer was transversely pre-cracked with saw every 3.5 m. The cracks made were sealed with bituminous emulsion, and the surface was protected with a bituminous curing coat (Figure 22.18).

Figure 22.18. Appearance of pre-cracking layer and soil-cement cover with curing emulsion.

The material quality control was conducted along the 591 meters of the section. Mainly focused on the material humidity that came from the plant, and over the reached densities after compaction. The results show the correct performance of the material. The target density was reached at the construction site (2.12 t/m^3), indicating that it would reach the 2.5 MPa required.

6.6. Final remarks

The use of industrial waste will increase over time, as non-renewable resources become increasingly scarce. But for these alternative materials to be visible, and their potential application to be demonstrated, real scale works, such as those shown in this chapter, are needed, which implies that companies, governments, and research entities are willing to carry out such advances.

The real scale work results shown here, like other research studies, that Waste Paper Fly Ash can be used in the construction industry as a hydraulic road binder, replacing lime or cement. It should also be mentioned that the ashes used in these large-scale tests have low variability in physical and chemical properties, helping to minimize errors when used on site.

After the exhaustive laboratory/field testing and pilot executions, it is proved the correct technical performance for WPFA-stabilized soils basis on standard stabilized-soil types of Spanish regulations. In all cases, the total amount of traditional binder (cement or lime) was entirely replaced by WPFA successfully.

The S-EST2, S-EST3, and SC layers were carried out with the same machinery and procedures of the traditional stabilized soils without any relevant effects in terms of productivity once it entered into continuous production. That is, after the initial start-up and dosing adjustments.

The most significant precaution on this material is its sensitivity to excess water during compaction, which drastically reduces its strength if the ash supply is very tight.

Environmentally, this type of execution reduces the consumption of raw materials and GHG emissions to the atmosphere produced by cement manufacture, being no potential risk for humans and the ecosystems if proper mixing, handling, and use during the construction process are followed. In addition, it fosters a Circular Economy model by taking advantage of a byproduct produced in industry and favors its commitment of "Zero Waste" to landfill.

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Chapter 7

7.1. Conclusions

Recycling pulp and paper generates various types of waste which can be used as fuel in fluidized bed combustion. The final product of this process is two types of ashes known as waste paper fly ash and bottom ash. Due to new regulations, dumping these ashes into the land is being restricted, hence a new way of dealing with these ashes is in need.

This research has focused mainly on the use of waste paper ash (WPA) as the binder in hydraulic roads, considering a full substitution of commonly used binders such as cement. Meanwhile, as WPA is a waste from paper and pulp manufacturing, its environmental impact is unknown. Thus, this research is also considered this aspect of the WPA utilization in civil engineering.

All the results from the mechanical standpoint to environmental and durability demonstrated that WPFA and WPBA can successfully be used as binders without the need of incorporating any other material. However, the basic principles regarding the stabilization of soil using WPFA should be followed, which can be defined as adding a 30 minutes delay time to WPFA for setting before compacting and decreasing the amount of water.

The variation of samples during a year collected from the recycling plant showed little difference. The chemical composition during a year showed that WPA was mainly composed of CaO, SiO, and Al_2O_3. The main minerals are lime, quartz, portlandite, calcium silicate, gehlenite, and halite. The particle size distribution showed very similarities between samples.

When the ashes (WPFA and WPBA) come into contact with water, a hydration reaction of the reactive compounds takes place, generating C-S-H and Friedel´s salt. The production of this last compound is due to the presence of chlorides in the ashes. Likewise, a production of portlandite is observed, which, as the curing process proceeds, will carbonate in the presence of CO_2.

The compressive strength results showed that both ashes can gain strength without incorporating any other substitute. However, these values for WPFA were higher than those of the WPBA. At 7 day, WPFA gained 57 % more strength, and at 56 days WPFA obtained 32% more strength than of WPBA. Lower reactivity of WPBA is due to a large particle size compared to WPFA and, possibly, to a lower amount of amorphous phase.

When it comes to the stabilization of soil using WPFA, some considerations should be taken into account. Firstly, WPFA expands when it becomes into contact with water. Secondly, increasing the water content in the mix also leads to lower strength. To avoid these problems, this research suggested adding a delay time after adding water to the mix (Soil +WPFA) and before compacting. The second suggestion is that decreasing water.

It was concluded that 30 minutes delay time and decreasing the optimum water content by one point of modified proctor gained the most strength among other water and delay time variations.

Finally, stabilisation of soil with WPFA and WPBA is possible and can be applied. The results of six different types of soil samples showed that WPFA and WPBA can gain strength without incorporating any other type of binder. Nevertheless, their use depends on the needed strength. Finally, WPBA should be used in subbase soil or when a low-performance base is needed.

From the environmental and utilisation perspective, the chemical properties of WPFA and WPBA can be altered depending on the material used during incineration, which can change the leaching properties of these ashes. The leaching test results showed that the level of barium should be considered when working with these ashes. The amount of barium decreased significantly when WPA was used as a binder (< 1.4 mg/kg). Moreover, the trial test demonstrated a slightly high amount of antimony, whereas the amount of barium was low. Besides, no environmental impact was observed at the depth of 2m. On comparing the results with the main metalloids concentration established in the European directive (Directive 1999/31/EC), the final product (soil + WPFA) can be categorised as an inert material.

7.2. Future lines of investigations

Given the limitations of the research programme carried out in this thesis, some suggestions for future research are proposed in order to complement the results obtained and conclusions.

The first and possibly the most important suggestion for future research is aimed at validating all the results obtained in this work using clay soils. All the soils studied in this research were classified as granular and sandy soils. Since clay soils exhibit different behaviour, such as higher reactivity due to their smaller particle size and chemical composition, it is possible that new reactions between soil and ashes (WPFA and WPBA) may be observed.

The second suggestion for further research is related to improving the reactivity of the WPBA. The low strength gain by WPBA is due to many factors that have a good potential to be studied. One of the factors can be coarser particle size compared to WPFA. Grinding to lower particle size may be helpful to reach higher strength.

As explained in Chapter 5, in Spain, there are large areas with expansive soils (due to the presence of gypsum) which is a problem for the durability of roads. Therefore, it is proposed to study soils with a higher gypsum contents (>5 %) than those studied in this research, in order to set gypsum content limits when using WPA. To have a better understanding of WPA, it should be compared to an ordinary Portland cement.

Lastly, due to the great importance of not polluting the environment, further research is needed to broaden the understanding of the environmental impact of the use of these ashes (WPFA and WPBA), as well as the mechanism of interaction between the ashes, soil and water.