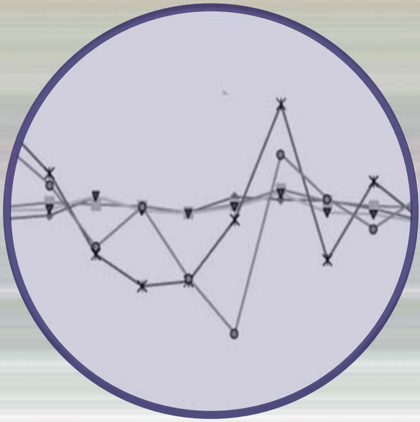

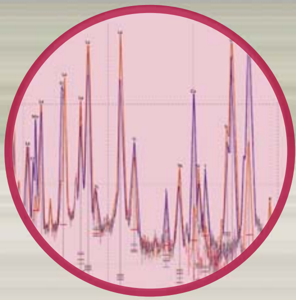

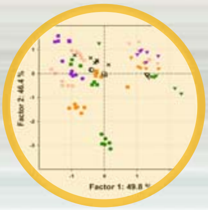

TESIS DOCTORAL

VIABILIDAD DE USO DE SUBPRODUCTOS INDUSTRIALES EN LA FABRICACIÓN DE MATERIALES EN BASE CEMENTO

FEASIBILITY USE OF INDUSTRIAL BY-PRODUCTS IN THE MANUFACTURE OF CEMENT-BASED MATERIALS

JULIA ROSALES GARCÍA

UNIVERSIDAD DE CÓRDOBA
Dep. de Ingeniería de Construcción

TITULO: *VIABILIDAD DE USO DE SUBPRODUCTOS INDUSTRIALES EN LA FABRICACIÓN DE MATERIALES EN BASE CEMENTO*

AUTOR: *Julia Rosales García*

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Campus de Rabanales
Ctra. Nacional IV, Km. 396 A
14071 Córdoba

https://www.uco.es/ucopress/index.php/es/
ucopress@uco.es

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Dña. Julia Rosales García

Para la obtención del

Título de Doctor con Mención Internacional por la Universidad de Córdoba

Director:

Dr. Francisco Agrela Sainz

Dr. Manuel Cabrera Montenegro

Córdoba, 2019

TÍTULO DE LA TESIS: VIABILIDAD DE USO DE SUBPRODUCTOS INDUSTRIALES EN LA FABRICACIÓN DE MATERIALES EN BASE CEMENTO.

DOCTORANDO: Julia Rosales García

INFORME RAZONADO DE LOS DIRECTORES DE LA TESIS

La generación y gestión de cualquier tipo de residuo constituye un problema ambiental grave en la sociedad actual. Así pues, la reducción de su generación y su adecuada gestión son necesarias para evitar graves impactos en el medio ambiente que provocan contaminación afectando a los ecosistemas y a la salud humana. En la actualidad el aumento de la conciencia en las consideraciones ambientales y, más recientemente, el concepto de desarrollo sostenible han conducido a un aumento en la reutilización y valorización de residuos.

La presente Tesis desarrolla previamente un estudio de la situación actual en relación a los tipos de residuos que son generados y acumulados en grandes cantidades, considerando parámetros actuales y analizando la evolución que puede producirse en el sector industrial. Analizada la situación, esta Tesis abarca el estudio de tres tipos de subproductos industriales generados y acumulados en grandes cantidades.

Uno de estos tipos de residuos es el generado por nuevas fuentes de energías renovables como la generación de electricidad a partir de la ***combustión de biomasa.*** En los últimos años se ha producido un crecimiento acelerado del uso de este producto para la generación de energía, y se prevé que su uso seguirá aumentado, siendo Andalucía líder en generación de electricidad a partir de biomasa. Aunque el uso de biomasa se considera energía limpia, la biomasa genera subproductos que se acumulan como las cenizas volantes y las cenizas de fondo. Debido a las altas tasas generadas y la escasez de estudios para su reutilización, la presente Tesis evalúa la viabilidad técnica de las cenizas de fondo de biomasa como material cementante para su aplicación como sustituto de materias primas en la fabricación de materiales en base cemento y como estabilizador de suelos.

Analizando el sector industrial actual, la ***producción de acero inoxidable*** es uno de los sectores más dinámicos de la industria manufacturera debido a un gran aumento del uso de este producto en los sectores de la construcción y la industria. Por cada tres toneladas de acero inoxidable producidas, se genera aproximadamente una tonelada de escorias que se acumula sin ningún tipo de valorización. En Andalucía se ubica la principal industria de acero inoxidable de España con producción a nivel mundial.

Siguiendo la línea marcada para la realización de la presente tesis, se evalúa el uso de las escorias de acero inoxidable generadas como material cementante en la fabricación de materiales en base cemento.

Finalmente, siguiendo con la evaluación de grandes cantidades de residuos acumulados, sin valorización y con la necesidad de encontrar un uso potencial posible que le dé un valor añadido para su reutilización; nos centramos en un foco con una gran repercusión ambiental, la ***acumulación de fosfoyeso*** existentes en las balsas de Huelva.

Centrándonos en los objetivos básicos marcados por esta Tesis, el uso de fosfoyeso como material regulador de fraguado en la fabricación de materiales en base cemento es un punto clave a estudiar.

El carácter innovador que presenta la Tesis, basándose en estudios de nuevos subproductos industriales para su aplicación como materiales cementantes que sustituyan materias primas utilizadas hasta la fecha, no deja de lado la aplicación de otro tipo de residuos ampliamente estudiados y cuyas características técnicas y viabilidad de aplicación en el sector de la ingeniería civil está demostrado.

De esta forma, mediante la presente Tesis, se desarrolla de forma combinada el estudio innovador del uso de subproductos industriales y la demostración y fomento de viabilidad de uso de residuos con características conocidas.

Este es el caso de los ***Residuos de Construcción y Demolición*** (RCD). La valorización de los RCD producidos está en incremento constante llegando así a cumplir los objetivos establecidos para el horizonte 2020, impulsando la mejora tecnológica en materia de aplicación de los áridos reciclados en infraestructuras.

Por lo que es fundamental seguir avanzando en estudios que promuevan su utilización en combinación con nuevos materiales.

Es por ello que esta Tesis está fundamentada en el concepto de ***"Valorización y Construcción Sostenible***", y durante el desarrollo experimental de la misma se ha tratado de abordar desde el punto de vista de la ingeniería, cuatro pilares fundamentales que permiten alcanzar dicho concepto: reducción de la utilización de recursos, potenciar residuos industriales, viabilidad técnica y conservación del medioambiente.

Estos pilares se han desarrollado de forma coherente a lo largo del transcurso de la misma que ha culminado con la publicación de cinco artículos en algunas de las revistas más prestigiosas en el área de materiales de construcción e ingeniería civil, tres de ellas en el primer cuartil:

1. **J. Rosales**, M.G. Beltrán, M. Cabrera, A. Velasco, F. Agrela (2016) ***Feasible use of biomass bottom ash as addition in the manufacture of lightweight recycled concrete.*** Waste and Biomass Valorization 7 953-963

2. **J. Rosales,** M. Cabrera, M.G. Beltrán, M. López, F. Agrela (2017) ***Effects of treatments on biomass bottom ash applied to the manufacture of cement mortars***. Journal of Cleaner Production 154 424-435.

3. **J. Rosales,** M. Cabrera, F. Agrela (2017) ***Effect of stainless steel slag waste as a replacement for cement in mortars. Mechanical and statistical study***. Construction and Building Materials 142 444–458.

4. M. Cabrera, **J. Rosales,** J. Ayuso, J. Estaire, F. Agrela (2018) ***Feasibility of using olive biomass bottom ash in the sub-bases of roads and rural paths.*** Construction and Building Materials 181, 266-275.

5. **J.Rosales**, S.M. Pérez, M. Cabrera, M.J. Gázquez, J.P. Bolivar, F. Agrela (2019).
   Phosphogypsum treated to be used as alternative set regulator and mineral addition in cement production. Construction and Building Materials. ***Under review***

Del mismo modo, como muestra de los avances y hallazgos realizados, se adjuntan 3 publicaciones en revistas indexadas, la participación en 2 capítulos de libro editado por Elsevier y 17 aportaciones a Congresos.

Para la realización de estos estudios se ha contado con la participación de investigadores externos a la Universidad de Córdoba, destacando la colaboración en el quinto trabajo del profesor Dr. Juan Pedro Bolívar y Dra. Silvia Pérez (Gupo de investigación FRYMA, Universidad de Huelva) y Dr. Manuel Gázquez (Departamento de Física Aplicada, Universidad de Cádiz).

Por tanto, la presente Tesis Doctoral cubre de forma exhaustiva todos los objetivos establecidos a priori respecto a la caracterización del comportamiento de subproductos industriales y propiedades cementantes (cenizas de fondo de biomasa, escorias de acero inoxidable y fosfoyeso), así como el análisis de sus posibles aplicaciones en ingeniería, estudiando su idoneidad en la fabricación de materiales en base cemento con combinación de otros residuos previamente estudiados (árido reciclados).

Por todo ello, se autoriza la presentación de la Tesis Doctoral "**Viabilidad de uso de subproductos industriales en la fabricación de materiales en base cemento**".

Córdoba, 14 de Enero de 2019

Firma de los directores:

Fdo.: Dr. Francisco Agrela Sainz

Fdo.: Dr. Manuel Cabrera Montenegro

Todo pasa y todo queda,
pero lo nuestro es pasar.

Pasar haciendo caminos…
Antonio Machado

A mis padres Fia y Manuel, por enseñarme el valor del compromiso y la importancia de las decisiones

A mis hermanos Manu y Fonfo, sin vosotros no habría ganas y alegría

A ti Archi, por compartirlo todo, por crear juntos

Agradecimientos

Quisiera dar mi más sincero agradecimiento a todas y cada una de las personas que han compartido este camino conmigo y han contribuido a que este proyecto tenga forma, sin ellos no hubiera sido posible llegar hasta aquí.

A mi director, Dr. Francisco Agrela Sainz por su confianza durante toda mi trayectoria investigadora, por sus ganas y su apoyo. Por creer siempre que era posible.

Quiero continuar agradeciendo a mi co-director de tesis, Dr. Manuel Cabrera Montenegro por su "múltiple función", has sido un apoyo fundamental en esta travesía de esfuerzo y dedicación. Por dedicarme tu tiempo, por tus palabras siempre precisas y adecuadas, por tu confianza. Gracias por ser referencia, amigo y compañero.

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Al área de Ingeniería de la Construcción de la Universidad de Córdoba, por proporcionar todo lo necesario, tanto en instalaciones, como en materiales, recursos, sabiduría y experiencia para hacer posible esta Tesis.

A la empresa Votorantim Cimentos y sobre todo a José Carlos Palma, Esther Flores y J. Antonio Herrera, que me han abierto las puertas de su conocimiento y experiencia, dándome la oportunidad de formarme profesionalmente y lo que es más importante, como persona.

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Agradezco al grupo de investigación FRYMA de la Universidad de Huelva su confianza e implicación en este proyecto, especialmente a Dr. Juan Pedro Bolívar, a Dr. Manuel Gázquez y a Dra. Silvia Pérez. Gracias por vuestro apoyo, vuestro tiempo y vuestra dedicación.

Vorrei anche ringraziare la Prof.ssa Valeria Corinaldesi dellÚniversità Politecnica delle Marche peer la accoglienza che mi ha offerto nel suo gruppo di ricerca, insegnandomi direttamente in laboratorio e mostrandomi nuove linee di lavoro. Grazie per il suo tempo, dedizione e supporto.

Alla mia piccola familia italiana che mi ha accolto durante i miei mesi di permanenza. Grazie a loro, é stato facile per me muovermi in una città sconosciuta. Sopratutto grazie a Giulia, Silvio, Vale e naturalmente a Eugenia, ti considero mia sorella. Grazie per esserti presa cura di me,ti ricordero sempre con un sorriso.

No olvidar a mis amigos. A los pradenses y al 41020, cada rato que pasamos juntos sirve de impulso para coger fuerzas, para reírnos de todo y como no, también para olvidarnos un poco de todo. Gracias zagales.

A mis amigas y "pequeños descendientes", por sus horas de escucha, por hacerme ver lo verdaderamente importante de las cosas, por estar siempre dispuestas, por las risas, los llantos, por sostenerme, por quererme. Gracias Mondragonas.

A Paca, Antonio y Verónica. Por todo su cariño, por la ayuda, por la confianza. Gracias.

A mi familia, Fía, Manuel, Manu y Fonfo. Por estar siempre, aunque sea lejos. Por apoyar todas mis decisiones y creer en mí, incluso más que yo. Por el entusiasmo mostrado en cada avance de esta Tesis (aunque no se enteraran de nada). No hay palabras para agradecer el apoyo que me dais, el cariño, las ganas. Gracias familia.

Y como no, a Archi y Balú. Por cada día. Por estar, por ser, por construir. Por haber comenzado y terminado esta etapa juntos. Por darlo todo. Gracias.

A todos, GRACIAS

Córdoba, 2019

Abstract

Although waste generation increases with technological development, progress also has a beneficial impact on waste and by-products reuse and management, in which specific applications are sought for these materials.

In this context, the research developed by this PhD thesis arises, whose objective is to analyze from the point of view of sustainability, the reuse of waste from different very powerful industrial sector in Andalusia, Spain and worldwide as a substitute for the raw materials used in the manufacture of cement-based materials. In this way, achieve the end of waste condition and classify them as by-products, demonstrating that the properties of these materials characterize them as potential raw materials for the manufacture of cement-based materials. This research focuses on the development of new and innovative cement-based materials that incorporate biomass bottom ash (BBA), recycled mixed aggregates (RMA), stainless steel slag waste (Sw) and phosphogypsum (PG) for their integral application in construction sector, analyzing its technical and environmental viability to maximize its use.

The work developed has as a first phase an extension of the knowledge of the feasibility of using RMA in combination with BBA in new materials. For the development of this first phase, a physical-chemical and environmental characterization of BBA is carried out. In addition to this an evaluation of the physical and mechanical properties of different mixtures of BBA and RMA were studied for the achievement of a cement-based material with technical characteristics which leads to a feasibility of valorisation of these waste. The results obtained lead to a more centralized research on the cementing properties of the BBA.

For this reason, in a second phase, BBA optimization through simple processing is proposed to applicate it as cementing material. An exhaustive characterization of these new materials produced through processing is carried out. In addition to this, the technical properties of the cement-based materials manufactured with the processed BBA were evaluated.

After the evaluation of the cementing properties of the CFB and having checked the pozzolanic capacity of the same, a third phase is carried out in which the application of this type of industrial by-product in the stabilization of soils is studied. This study shows that the use of CFB as a soil stabilizer is viable, improving the mechanical properties and loading capacity of clay soils

In a quarter phase, and following the proposed line of research, a second industrial waste was analysed (Sw). Developing the research as in the second phase, in which an extensive study of the properties of this waste and its different processes were carried out and the technical characteristics of the new materials manufactured with EAI as a cement substitute were evaluated. This study shows in a clear and innovative way the potential of this waste for its application in the cement industry.

Finally, after the analysis of all results obtained, the study of a third industrial waste is developed. This waste (PG) is accumulated in large quantities without any viability of use. Following the methodology, a broad characterization of the waste with various treatments was carried out. The evaluation of the technical and environmental properties of the new cement-based materials manufactured with this industrial waste leads to the verification of the feasibility of reuse as a regulating material for setting and mineral addition with cementing properties.

The results obtained show the potential of industrial waste as a substitute for raw materials in the manufacture of cement-based materials. Demonstrating the feasibility of use as cementing material from the scientific and technological point of view.

Resumen

La generación de residuos se incrementa según avanza el desarrollo tecnológico de las sociedades. Sin embargo, este progreso también repercute de forma positiva en la gestión y reutilización de los residuos y subproductos generados, de forma que se busquen aplicaciones concretas al uso de los mismos.

En este contexto, surge la investigación desarrollada por la presente Tesis Doctoral, cuyo objetivo es analizar desde el punto de vista de la sostenibilidad, la reutilización de residuos procedentes de diferentes focos industriales muy potentes en Andalucía, España y a nivel mundial como sustitutivo de las materias primas utilizadas en la fabricación de materiales en base cemento. Para de esta forma, conseguir el fin de condición de residuo y catalogarlos como subproductos, demostrando que las propiedades de los mismos los caracterizan como materias primas potenciales para la fabricación de materiales en base cemento. Esta investigación se centra en el desarrollo de nuevos e innovadores materiales base-cemento que incorporan cenizas de fondo de biomasa (CFB), áridos reciclados mixtos (ARM), escorias de acero inoxidable (EAI) y fosfoyeso (FY) para su aplicación integral en construcción, analizando su viabilidad técnica y ambiental para potenciar su uso.

El trabajo desarrollado, tiene como primera fase una ampliación del conocimiento de la viabilidad de uso de ARM en combinación con CFB en nuevos materiales. Para el desarrollo de esta primera fase se lleva a cabo una caracterización físico-química y ambiental de las CFB y una evaluación de las propiedades físicas y mecánicas de diferentes mezclas de CFB y ARM para la consecución de un material en base cemento con características técnicas que lleve a una viabilidad de valorización de estos residuos. Los resultados obtenidos llevan a desarrollar de manera más amplia las propiedades cementantes de la CFB.

Para ello, en una segunda fase, se propone la optimización de las CFB como material cementante mediante procesamientos sencillos. Se lleva a cabo una caracterización exhaustiva de estos nuevos materiales producidos a través

del procesamiento y se evalúa las propiedades técnicas adquiridas por materiales en base cemento fabricados, demostrando la viabilidad de uso de CFB con tratamientos sencillos en la fabricación de morteros como material sustitutivo del cemento.

Tras la evaluación de las propiedades cementantes de las CFB y habiéndose comprobado la capacidad puzolánica de las mismas, se lleva a cabo una tercera fase en la que se estudia la aplicación de este tipo de residuos en la estabilización de suelos. Este estudio muestra que es viable el uso de CFB como estabilizador de suelos mejorando las propiedades mecánicas y capacidad de carga de suelos arcillosos.

En una cuarta fase, y siguiendo con la línea de investigación propuesta, se analiza un segundo residuo, EAI. Desarrollando la investigación como en la segunda fase, en la que se realiza un amplio estudio de las propiedades de este material y sus diferentes procesamientos y se evalúan las características técnicas de los nuevos materiales fabricados con EAI como sustituto de cemento. Este estudio muestra de forma clara e innovadora el potencial de este residuo para su aplicación en la industria cementera.

Por último, tras el análisis de todos los resultados obtenidos, se desarrolla el estudio de un tercer residuo industrial sin ninguna viabilidad de uso y acumulado en grandes cantidades, FY. Siguiendo la metodología se lleva a cabo una amplia caracterización del material con diversos tratamientos. La evaluación de las propiedades técnicas y ambientales de los nuevos materiales en base cemento fabricados con este residuo industrial llevan a la comprobar la viabilidad de reutilización como material regulador de fraguado y adición mineral con propiedades cementantes.

Los resultados obtenidos ponen de manifiesto el potencial de los residuos industriales como sustituto de materias primas en la fabricación de materiales en base cemento. Demostrando la viabilidad de uso como material cementante desde el punto de vista científico y tecnológico.

ÍNDICE

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Abreviaturas

ARM	Árido Reciclado Mixto
BBA	Biomass Bottom Ash
BBA-C	Biomass Bottom Ash Crushed
BBA-C-CO	Biomass Bottom Ash Crushed and Combusted
BBA-C-CO-NL	Biomass Bottom Ash Crushed, Combusted and without lightweight particles
BBA-C-NL	Biomass Bottom Ash Crushed and without lightweight particles
BBA-CO	Biomass Bottom Ash Combusted
BBA-CO-NL	Biomass Bottom Ash Combusted and without lightweight particles
BBA-NL	Biomass Bottom Ash without lightweight particles
BFA	Biomass Fly Ash
Bi	Binder intensity indicator
BOF	Basic Oxygen Furnace
CB	Cenizas Biomasa
CBR	California bearing ratio
CDW	Construction and Demolition Waste
CEM	Cement
CFB	Cenizas de Fondo de Biomasa
CK	Clinker
CS	Compressive Strength
CVB	Cenizas Volantes de Biomasa
DMR	DIRECTIVA 2008/98/CE

EAF	Electric Arc Furnace
EAI	Escoras de Acero Inoxidable
EC	Expanded clay
ECS	Expansive clay soil
EDXRF	X-Ray Fluorescence Spectrometry
EHE	Instrucción Hormigón Estructural
EPS	Polystyrene Foam
FA	Fly Ash
FS	Flexural Strength
FY	Fosfoyeso
LER	Listado Europeo de Residuos
LOI	Loss on ignition
LWC	Lightweight Concrete
MAGRAMA	Ministerio de Agricultura, Alimentación y Medio Ambiente
MLR	Multiple Linear Regression Model
NA	Natural Aggregates
NG	Natural Coarse Gravel
NG	Natural Gypsum
NS	Natural Sand
OECD	Organisation for Economic Cooperational and Development
OPC	Ordinary Portland Cement
PCA	Principal Components Analysis
PEMAR	Plan Estatal Marco de Gestión de Residuos
PG	Phosphogypsum

PG-3	Pliego de Prescripciones Técnicas Generales para Obras de Carreteras y Puentes
PG-B	Phosphogypsum Burned
PG-C	Phosphogypsum Crushed
PG-NP	Phosphogypsum non-processed
PG-W	Phosphogypsum Washed
PNIR	Plan Nacional Integrado de Residuos
QL	Quicklime
QXRD	Quantitative X-ray diffraction
RCD	Residuos de Construcción y Demolición
RCD-ARM	Residuos de Construcción y Demolición. Árido Reciclado Mixto
RMA	Recycled Mixed Aggregates
SEM	Scanning Electron Microscopy
SH	Shrinkage
SNS	Standard Natural Sand
SP	Super-Plasticiser
SSD	Saturated Surface Dry
SW	Stainless Steel Slag Waste
SW-B	Stainless Steel Slag Burned
SW-C	Stainless Steel Slag Crushed
SW-CB	Stainless Steel Slag Crushed and Burned
SW-N	Stainless Steel Slag Waste non-processed
UE	Unión Europea
UPV	Ultrasonic Pulse Velocity
XRD	X-Ray Diffraction Analysis

COMPENDIO DE PUBLICACIONES

La realización de investigaciones tiene como interés principal la búsqueda de su justificación. Para la sociedad, la divulgación científica es un pilar fundamental para dar conocimiento, comprender, enseñar, dar respuesta y generar soluciones a problemas planteados. El intercambio de conocimiento entre la comunidad investigadora y la sociedad es esencial para el desarrollo y evolución.

Siguiendo la directriz marcada anteriormente, La siguiente tesis consiste en un "***compendio de publicaciones***", según la Universidad de Córdoba ("*Articulo 24 de La Normativa Reguladora de los Estudios de Doctorado por la Universidad de Córdoba*") sobre viabilidad de uso de subproductos industriales en materiales en base cemento. Además, la presente Tesis Doctoral cumple con los requisitos para optar al título de ***Doctor con Mención Internacional*** de acuerdo con el *Articulo 35 de La Normativa Reguladora de los Estudios de Doctorado por la Universidad de Córdoba*.

Este capítulo incluye diferentes aportaciones derivadas directamente de la presente Tesis Doctoral.

- PUBLICACIÓN 1. FEASIBLE USE OF BIOMASS BOTTOM ASH AS ADDITION IN THE MANUFACTURE OF LIGHTWEIGHT RECYCLED CONCRETE.

  - **Authors:** Rosales, J., Beltrán, M. G., Cabrera, M., Velasco, A., & Agrela, F.
  - **Reference:** Waste and Biomass Valorization, Vol.: 7; Num.: 4;Pag.: 953-963; AUG 2016
  - **Quality indicators:** *Impact Factor: 1,874 / Category Environmental Sciences 131/241 Q3*
  - **DOI:** *https://doi.org/10.1007/s12649-016-9522-4*
  - **Abstract:**

Biomass is a renewable energy source that is increasingly being used worldwide. However, because of recent increases in production, waste products from biomass combustion are becoming a relevant environmental and economic problem. Other wastes from the construction and demolition sectors have been extensively studied. For this, several research studies have been performed to study the mechanical and some durability properties in concrete manufacturing with recycled concrete and mixed aggregates from different construction origins.

In previous works, the lower density of recycled mixed aggregates (RMA) and biomass bottom ash (BBA) with respect to natural aggregates was studied. This feature can be exploited for the production of construction elements that require the use of low-density materials, such as lightweight concrete. For this, the aim of this work was to study the influence of the use of recycled mixed aggregates and biomass bottom ash, as replacements for the natural aggregates, on the mechanical behaviour, durability properties and environmental risk of recycled lightweight concrete. Several replacements for natural aggregates through recycled aggregates and biomass bottom ash were applied in the manufacture of lightweight concretes. To study the concrete behaviour, properties such as density, absorption, compressive strength, flexural strength, UPV, water penetration and drying shrinkage were measured. Due to the incorporation of RMA and BBA, a decrease of the density and mechanical properties of the recycled concrete manufactured was obtained with respect to the control mix.

Therefore, the results showed the possibility of applying these types of recycled materials in lightweight concretes for their application in specific constructive elements.

Through this study the possibility of reuse of waste and industrial by-products (RMA and BBA) that have so far been accumulated mainly in landfill is demonstrated. The positives results show the possibility of manufacture of lightweight concrete with these by-products, achieving a material with a lower density and mechanical requirements that comply with the current standards for concrete.

- PUBLICACIÓN 2. FEASIBILITY OF USING OLIVE BIOMASS BOTTOM ASH IN THE SUB-BASES OF ROADS AND RURAL PATHS.
  - **Authors:** Cabrera, M., Rosales, J., Ayuso, J., Estaire, J., & Agrela, F.
  - **Reference:** Construction and Building Materials, Vol.: 181;Pag.: 266-265; AUG 2018
  - **Quality indicators:** *Impact Factor: 3,485 / Category Civil Engineering 11/128 Q1*
  - **DOI:** *https://doi.org/10.1016/j.conbuildmat.2018.06.035*
  - **Abstract:**

Clay soils are widely distributed throughout the world and are the source of multiple technical problems in their application for the construction of sub-grade and sub-road bases. These types of soils are found in areas where civilian infrastructure such as roads and rural roads must be built. Therefore, in many situations it is necessary to use stabilized expansive soils, in the formation of the foundation and structural layers of linear infrastructures.

Soil stabilization is used to increase the load capacity of the soil, and mixtures of lime and cement are generally used as binders.

In recent years, interest in the recycling of industrial products and by-products has increased. One example of this is the use of biomass combustion in power plants. The management of significant amounts of waste (biomass bottom ash) from biomass power plants remains a problem.

This paper presents the results of an experimental study for stabilizing expansive soil to determine its bearing capacity and mechanical properties via a triaxial test of the addition of biomass bottom ash. A double objective was targeted: reduction of the problems in using this type of soil and provision of a use for this type of waste. The results showed significant improvements in the mechanical. Therefore, herein is proposed the use of biomass bottom ash as a stabilizing agent for expansive soils, to improve the efficiency of the construction process by incorporating this product into a second life cycle as road bases.

- PUBLICACIÓN 3. EFFECTS OF TREATMENTS ON BIOMASS BOTTOM ASH APPLIED TO THE MANUFACTURE OF CEMENT MORTARS.

  - **Authors:** Rosales, J., Cabrera, M., Beltrán, M.G., López, M., & Agrela
  - **Reference:** Journal of Cleaner Production; Vol.: 154; Pag.: 424-435; JUN 2017
  - **Quality indicators:** *Impact Factor: 5,651 / Category Environmental Engineering 7/50 Q1*
  - **DOI:** *https://doi.org/10.1016/j.jclepro.2017.04.024*
  - **Abstract:**

The use of biomass for power generation is increasingly common. However, one of the most important problems when using biomass is the amount of waste produced in the combustion process such as ash, which must be transported to landfills for deposition.

Biomass bottom ash may contain a large amount of organic matter which is the most restrictive property for reusing this by-product. The potential reuse is determined by chemical and physical properties. The presence of light particles and organic matter confer to biomass bottom ash certain physical and chemical characteristics which significantly reduce the possibility of reuse. Previous studies have demonstrated the possibility of using biomass bottom ash in cement-treated materials, but its properties imply a decrease of compressive and flexural strength.

Therefore, this paper reported the study of the mechanical and durability properties of mortars containing biomass bottom ash applying different processing methods. Cement was replaced with different rates of substitution of biomass bottom ash and several samples were treated applying different techniques, such as grinding, elimination of lightweight particles and combustion.

The results showed significant improvements in the mechanical and durability properties of mortars in which some treatment were applied. Lightweight particle extraction and organic matter removal by burning considerably improved the mechanical behaviour of the manufactured mortars. Therefore, mortars with crushed biomass bottom ash without floating particles and without organic matter led to a 10% of compressive strength decrease with respect to the control mortar.

Thus, this study displays a possibility of waste valorisation by means of to the reuse of this type of by-product in mortars and concretes manufacture.

- <u>PUBLICACIÓN 4.</u> EFFECTS OF STAINLESS STEEL SLAG WASTE AS A REPLACEMENT FOR CEMENT IN MORTARS. MECHANICAL AND STATISTICAL STUDY.

- Authors: <u>Rosales, J.</u>, Cabrera, M., & Agrela
- Reference: Construction and Building Materials 42; Pag.: 444-458; JUL 2017
- Quality indicators: *Impact Factor: 3,485 / Category Civil Engineering 11/128 Q1*
- DOI: *https://doi.org/10.1016/j.conbuildmat.2017.03.082*
- Abstract:

This document studies replacing cement by stainless steel slag waste and improving the mechanical properties of the slag waste by using different types of treatments.

The application of stainless steel slag waste reduces the use of raw materials for manufacturing cement and provides a profit from the large amount of waste generated.

This study analyses the cementation and pozzolanic reaction characteristics of stainless steel slag waste to evaluate its strength activity index and its environmental impact. The cement was replaced with different substitution percentages of untreated stainless steel slag waste and slag waste that was processed through crushing, burning and both treatment to determine the optimum replacement ratio according to its mechanical properties. A study based on multivariate factor analysis was developed to compare these processed wastes according to their mechanical behaviour. The decision mechanism consists of a feature extraction method to evaluate the wastes used as a cement substitute.

Otro artículo está actualmente bajo revisión:

- PUBLICACIÓN 5. PHOSPHOGYPSUM TREATED TO BE USED AS ALTERNATIVE SET REGULATOR AND MINERAL ADDITION IN CEMENT PRODUCTION
    - Authors: Rosales J., Pérez S.M., Cabrera M., Gázquez M.J., Bolivar J.P., Agrela F.
    - Reference: Construction and Building Materials; Under Review
    - Quality indicators: *Impact Factor: 3,485 / Category Civil Engineering 11/128 Q1*
    - DOI: Under Review
    - Abstract:
Different treatments on phosphogypsum samples extracted in Huelva, Spain, different curing conditions and different percentage of addition were studied to evaluate the possibilities of being used as set regulator and as supplementary cement material to improve the mechanical behaviour of cement mortars.
The physical-chemical properties, mechanical behaviour and environmental impact of these phosphogypsum-based cement mortars were determined.
It was concluded that the phosphogypsum treatments and curing conditions influence the mineralogical transformations of mortars and therefore also the mechanical behaviour of the mortars tested. In addition, the heavy metal impurities in the phosphogypsum were immobilized in the cement matrix. Obtaining a clear improvement in the technical properties of cement mortars made with this waste compared to the traditional use of natural gypsum.

Otras publicaciones derivadas de la Tesis Doctoral:

- FEASIBLE USE OF BIOMASS BOTTOM ASH IN THE MANUFACTURE OF CEMENT TREATED RECYCLED MATERIALS.
  - **Authors:** *Cabrera, M., Agrela, F., Ayuso, J., Galvin, A. P., & Rosales, J.*
  - **Reference:** *Materials and Structures*, Vol.: 49; Isuue:18; Pag.: 3227-3238; AUG 2016
  - **Quality indicators:** *Impact Factor: 2,271 / Category Civil Engineering 31/128 Q1*
  - **DOI:** https://doi.org/10.1617/s11527-015-0715-2
  - **Abstract:**

A focus on environmental sustainability during the last decade has led to greater use of recycled aggregates to reduce the exploitation of existing reserves. In addition, environmentally consciousness has led to an increased use of renewable energy. Biomass is an important source of energy, and it also leads to high generation of waste products from biomass combustion. Previous studies have investigated the use of recycled aggregates from construction and demolition in road bases and sub-bases with positive results. This paper aims to study the feasibility of incorporating biomass bottom ash produced in the combustion process mixed with natural aggregates and recycled aggregates for use in civil engineering. The analysis of the mechanical properties was positive, showing the ability to use biomass bottom ash mixed with natural or recycled aggregates in specified ratios. Valuing biomass bottom ash can reduce waste generation and may lead to economic and environmental benefits.

- PROPERTIES OF RECYCLED CONCRETE MANUFACTURING WITH ALL-IN RECYCLED AGGREGATES AND PROCESSED BIOMASS BOTTOM ASH.
  - **Authors:** Agrela, F., Beltran, M. G., Cabrera, M., López, M., Rosales, J., & Ayuso, J.
  - **Reference:** *Waste and Biomass Valorization*, Vol.: 49; Num.:7; Pag.: 1247-1259; JUL 2018
  - **Quality indicators:** *Impact Factor: 1,874 / Category Environmental Sciences 131/241 Q3*
  - **DOI:** *https://doi.org/10.1007/s12649-017-9880-6*
  - **Abstract:**

Recycled aggregates (RA) have been extensively studied in the production of concrete. Normally, the coarse fraction of recycled concrete aggregates (RCA) is the most commonly used to manufacture recycled concretes. The manufacturing of concrete with fine fraction of

RCA and/or recycled mixed aggregates (RMA) (from a mix of concrete, asphalt, masonry, etc.) has not been studied in depth. In most cases, the recycling plants produce RA with an ALL-IN particle size distribution. These recycled materials could be named as ALL-IN RECYCLED CONCRETE AGGREGATES (aiRCA) and ALL-IN RECYCLED MIXED AGGREGATES (aiRMA). Applying these aiRCA or aiRMA, limiting the percentage of the substitution of natural aggregates (NA) by the aiRCA, is more beneficial for both the production costs and the environment. In recent studies, other by-products, such as biomass bottom ash (BBA) were used in concretes, substituting natural sand (NS) and improving the mechanical properties in concretes with low quantities of cement. It is possible to improve the properties of the BBA via mechanical processes (like screening or flotation) to reduce the organic matter content and there by obtain processed BBA (Pr-BBA). This study provides interesting data on the mechanical and durability properties of the concretes manufactured with 30% aiRCA and aiRMA, and also by applying different replacement rates (0, 15, and 30%) of NA by BBA and Pr-BBA. The mechanical and durability properties were analysed over different time durations in different mixtures. It was demonstrated that it is possible to apply these recycled materials in non-structural concrete mixtures by limiting the replacement rate. The application of BBA and Pr-BBA reduced the properties of the concrete. However, this reduction was less significant with the use of Pr-BBA.

- UPSCALING THE POLLUTANT EMISSION FROM MIXED RECYCLED AGGREGATES UNDER COMPACTION FOR CIVIL APPLICATIONS.
  - Authors: *Galvín, A. P., Ayuso, J., Barbudo, A., Cabrera, M., López-Uceda, A., & Rosales, J.*
  - Reference: *Environmental Science and Pollution Research, DEC 2017*
  - Quality indicators: *Impact Factor: 2,800 / Category Environmental Sciences 82/241 Q2*
  - DOI: *https://doi.org/10.1007/s11356-017-1017-8*
  - Abstract:

In general terms, plant managers of sites producing construction wastes assess materials according to concise, legally recommended leaching tests that do not consider the compaction stage of the materials when they are applied on-site. Thus, the tests do not account for the real on-site physical conditions of the recycled aggregates used in civil works (e.g., roads or embankments).
This leads to errors in estimating the pollutant potential of these materials. For that reason, in the present research, an experimental procedure is designed as a leaching test for construction materials under compaction. The aim of this laboratory test (designed specifically for the

granular materials used in civil engineering infrastructures) is to evaluate the release of pollutant elements when the recycled aggregate is tested at its commercial grain-size distribution and when the material is compacted under on-site conditions. Two recycled aggregates with different gypsum contents (0.95 and 2.57%) were used in this study. In addition to the designed leaching laboratory test, the conventional compliance leaching test and the Dutch percolation test were performed.

The results of the new leaching method were compared with the conventional leaching test results. After analysis, the chromium and sulphate levels obtained from the newly designed test were lower than those obtained from the conventional leaching test, and these were considered more seriously pollutant elements. This result confirms that when the leaching behaviour is evaluated for construction aggregates without density alteration, crushing the aggregate and using only the finest fraction, as is done in the conventional test (which is an unrealistic situation for aggregates that are applied under on-site conditions); the leaching behaviour is not accurately assessed.

Participación en Capítulos de Libro editado por Elsevier:

- CHAPTER 7. STEEL SLAGS.
  - Authors: *Thomas C., Rosales J., Polanco J. A., & Agrela F.*
  - Book: *New Trends in Eco-Efficient and Recycled Concrete.*
  - ISBN: *978-0-08-102480-5*
  - DOI: *https://doi.org/10.1016/B978-0-08-102480-5.00007-5*

- CHAPTER 13. APPLICATION OF ALKALI-ACTIVATED INDUSTRIAL WASTE.
  - Authors: *Payá J., Agrela F., Rosales J.,Martín Morales M., & Borrachero M.V.*
  - Book: *New Trends in Eco-Efficient and Recycled Concrete.*
  - ISBN: *978-0-08-102480-5*
  - DOI: *https://doi.org/10.1016/B978-0-08-102480-5.00013-0*

Otra difusión de los resultados obtenidos ha tenido lugar a través de diferentes congresos internacionales y nacionales, jornadas y seminarios como:

- INFLUENCE OF LIGHT AND NOT-COMBUSTED PARTICLES ON THE MECHANICAL AND DURABILITY MORTARS MADE WITH BIOMASS BOTTOM ASH.
  - Authors: *M. G. Beltrán, F. Agrela, M. Cabrera, J. Rosales, C. Dorado*
  - Type of publication: *Conference paper*
  - Reference: *Conference on Industrial Waste & Wastewater, Treatment & Valorisation. Greece, 21-23 May 2015*

- APPLICATION OF STAINLESS STEEL SLAG WASTE AS A PARTIAL REPLACEMENT TO MANUFACTURE CEMENT MORTARS.
  - Authors: *J. Rosales, F. Agrela, M. Cabrera, M. G. Beltrán, J. Ayuso.*
  - Type of publication: *Conference paper*
  - Reference: *Conference on Industrial Waste & Wastewater, Treatment & Valorisation. Greece, 21-23 May 2015*

- CEMENT TREATED RECYCLED MATERIALS MANUFACTURE WITH ADDITIONS OF BIOMASS BOTTOM ASH.
  - Authors: *M Cabrera., F. Agrela, J. Rosales, J. Ayuso*
  - Type of publication: *Conference paper*
  - Reference: *Resource Efficiency in Construction. 9th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials. Santander 10-12 June 2015 / ISBN: 978-84-606-8423-7*

- ENVIRONMENTAL IMPACT OF CEMENT TREATED RECYCLED MATERIALS MADE WITH BIOMASS BOTTOM ASH.
  - Authors: *M. Cabrera, F. Agrela, J. Rosales , A.P. Galvín*
  - Type of publication: *Conference paper*
  - Reference: *Resource Efficiency in Construction. 9th International Conference on the Environmental and Technical Implications of Construction with Alternative Materials. Santander 10-12 June 2015 / ISBN: 978-84-606-8423-7*

- PROPERTIES OF LIGHTWEIGHT CONCRETE MANUFACTURED WITH RECYCLED MIXED AGGREGATES.
  - Authors: *F. Agrela, J.Rosales, M.G.Beltrán, M. Cabrera, J. Ayuso*
  - Type of publication: *Conference paper*
  - Reference: *III International RILEM conference on progress of recycling in the built environment. Sao Paul, Brasil 3-5 August 2015 / ISBN: 9781510822504*

- STUDY OF RECYCLED AGGREGATES MANUFACTURED WITH BIOMASS BOTTOM ASH FOR APPLICATION IN CEMENT TREATED GRANULAR MATERIALS.
  - Authors: *M. Cabrera, F. Agrela, J. Rosales, C. Dorado, A.P. Galvin*
  - Type of publication: *Conference paper*
- Reference: *III International RILEM conference on progress of recycling in the built environment. Sao Paulo, Brasil 3-5 August 2015 / ISBN: 9781510822504*

- FEASIBLE USE OF BIOMASS BOTTOM ASH IN THE MANUFACTURE OF CEMENT-BASED MATERIALS.
  - Authors: *J. Rosales, M. Cabrera, C. Dorado, J. Ayuso, F. Agrela*
  - Type of publication: *Conference paper*
  - Reference: *9th International Concrete Conference at Dundee. Dundee, Scotland 4-6 July 2016 / ISBN: 9780957326316*

- PROPIEDADES TÉCNICAS Y MEDIOAMBIENTALES DE LOS ÁRIDOS RECICLADOS MIXTOS SEGÚN SU CLASIFICACIÓN.
  - Authors: *M. Cabrera, F. Agrela, J. Rosales, H. Cano*
  - Type of publication: *Conference paper*
  - Reference: *10º Simposio Nacional de Ingeniería Geotécnica. A Coruña, España 19-20 Octubre 2016.*

- REUSE OF AGGREGATES FROM RECYCLED CONSTRUCTION AND DEMOLITION WASTE COMMONLY DISPOSED IN LANDFILL.
  - Authors: *M. Cabrera, J. Rosales, F. Agrela*
  - Type of publication: *Conference paper*
  - Reference: *5th International Conference on Sustainable Solid Waste Management. Athen, Greece 21-24 June 2017.*

- INFLUENCE OF PHOSPHOGYPSUM AS SETTING REGULATOR ON THE MECHANICAL PERFORMANCES OF CEMENT MORTAR.
  - Authors: *J. Rosales, M. Cabrera S.M. Pérez, F. Mosqueda, M.J. Gázquez, J.P. Bolívar, F. Agrela*
  - Type of publication: *Conference paper*
  - Reference: *5th International Conference on Sustainable Solid Waste Management. Athen, Greece 21-24 June 2017.*

- PHYSICO-CHEMICAL AND RADIOLOGICAL CHARACTERIZATION OF PHOSPHOGYPSUM FOR ITS VALORIZATION IN CEMENT MORTAR.
    - Authors: *S.M Pérez., J. Rosales, M. Cabrera, F. Mosqueda, M.J. Gázquez, F. Agrela, J.P. Bolívar*
    - Type of publication: *Conference paper*
    - Reference: *5th International Conference on Sustainable Solid Waste Management. Athen, Greece 21-24 June 2017.*

- STABILIZATION OF EXPANSIVE MATERIAL WITH BIOMASS BOTTOM ASH. CBR BEHAVIOUR AND TRIAXIAL TEST.
    - Authors: *M. Cabrera., J. Rosales, A.P. Galvín, A. Barbudo, F. Agrela*
    - Type of publication: *Conference poster*
    - Reference: *5th International Conference on Sustainable Solid Waste Management. Athen, Greece 21-24 June 2017.*

- ESTUDIO DE APLICACIÓN DE ESCORIAS DE ACERO INOXIDABLE EN CEMENTOS Y MORTEROS.
    - Authors: *J. Rosales, M. Cabrera., F. Agrela, M.C.Janeiro,R. Ruiz, E. Quirós, P. Acosta, J. Almagro*
    - Type of publication: *Conference poster*
    - Reference: *Jornadas Nacionales sobre Aplicación e Innovación de Áridos Siderúrgicos y Escorias. Madrid, España 15-17 November 2017.*

- STAINLESS STEEL SLAG WASTE AS A REPLACEMENT FOR CEMENT IN MORTARS.
    - Authors: *F. Agrela, J. Rosales, M. Cabrera*
    - Type of publication: *Conference paper*
    - Reference: *5th International Conference on Recycling and Waste Management. London, UK 05-06 March 2018*

- FEASIBLE USE OF GLASS WASTE ELECTRICAL AND RECYCLED AGGREGATES IN CEMENT-TREATED MATERIALS.
    - Authors: *M. Cabrera, J. Rosales, A. Barbudo, A.P. Galvín, F. Agrela*
    - Type of publication: *Conference poster*
    - Reference: *International Conference of Environmental, Green Technology and Engineering. Cáceres, Spain 18-20 June 2018.*

- INDUSTRIAL BY-PRODUCTS AS SUPPLEMENTARY CEMENTING MATERIALS IN THE MANUFACTURE OF CEMENT MORTARS.
    - Authors: *J. Rosales, M. Cabrera, F. Agrela*
    - Type of publication: *Conference paper*
    - Reference: *IV Progress of Recycling in the Built Environment. Lisbon, Portugal 11-12 October 2018.*

- BIOMASS BOTTOM ASH A SUSTAINABLE ALTERNATIVE FOR THE MANUFACTURE OF CEMENT-BASED MATERIALS
    - Authors: *M. Cabrera, J. Rosales, F. Agrela*
    - Type of publication: *Conference paper*
    - Reference: *IV Progress of Recycling in the Built Environment. Lisbon, Portugal 11-12 October 2018.*

CAPÍTULO I

INTRODUCCIÓN

INTRODUCCIÓN

La sostenibilidad en la construcción y la ingeniería civil es la optimización de las actividades de construcción de forma que no tenga efectos nocivos sobre los recursos, el entorno y el ecosistema vivo. Es una forma de minimizar los impactos ambientales dañinos en la construcción.

Analizando la generación de residuos industriales en el ámbito nacional y evaluando las grandes cantidades que se disponen en vertedero se lleva a cabo la presente Tesis Doctoral para poder aumentar los porcentajes de reutilización de los materiales en estudio (áridos reciclados mixtos, cenizas de fondo de biomasa, escorias de acero inoxidable y fosfoyeso) y en consecuencia, poder llegar a los mínimos de reutilización y valorización impuestos por la normativa europea y nacional. Se plantea destinar estos materiales como sustitutos de materias primas utilizadas convencionalmente en la fabricación de materiales en base cemento para aplicaciones de ingeniería.

Esta investigación se basa en la ampliación del estado de conocimiento de residuos previamente estudiados por diversos autores pero escasamente aplicados, para potenciar su utilización en materiales en base cemento (RCD-ARM). Además de ello, se profundiza en el estudio de las propiedades de otros subproductos minoritariamente estudiados para evaluar su capacidad cementante y su viabilidad de uso en diferentes aplicaciones (CFB). Finalmente, y basándonos en el estudio de generación de residuos en España y especialmente en Andalucía y analizando las tasas de generación de los mismos, se lleva a cabo la evaluación de residuos escasamente estudiados (EAI y FY). Analizando su potencial como material cementante y su posible utilización en la fabricación de cemento como sustituto de materias primas tradicionales.

La demostración de la viabilidad de uso de estos residuos se lleva a cabo mediante un estudio de sus propiedades físico-químicas y una evaluación de las características tecnológicas de los materiales en base cemento fabricados con los mismos. Así como, un estudio medioambiental para cerrar el ciclo demostrativo.

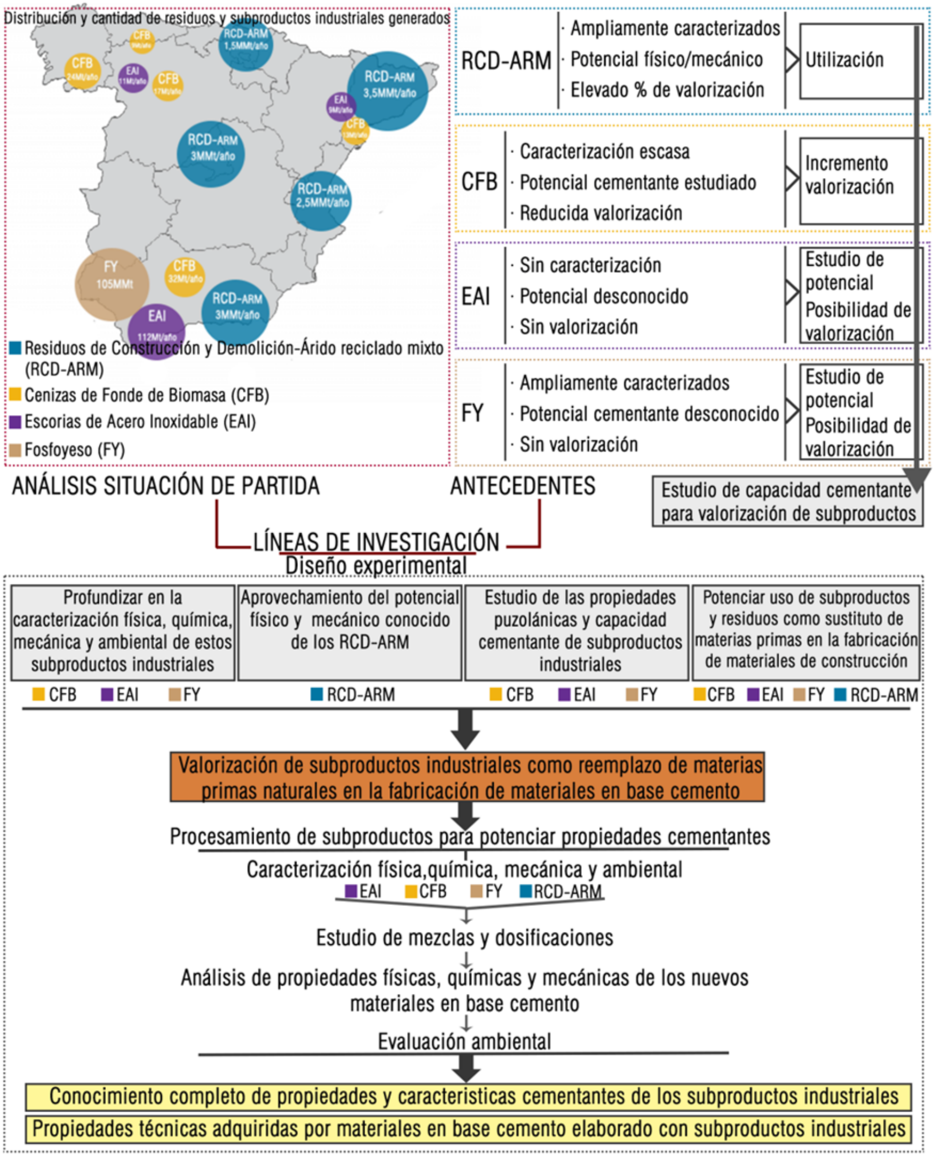


Figura 1.1: Esquema procedimental de investigación desarrollada

Capítulo II

ESTADO DEL ARTE

ESTADO DEL ARTE

***Construcción Sostenible**. Uso eficiente de energía, recursos naturales y nuevos materiales no perjudiciales para el medioambiente.*

- *RE-UTILIZACIÓN*
- *RE-CICLAJE*
- *RE-DUCCIÓN residuos*

Tanto el crecimiento demográfico, como el desarrollo tecnológico e industrial conllevan un aumento progresivo de generación de residuos. Se hace cada vez más evidente que nuestra sociedad debe ser una "sociedad para el reciclado"[1]. La producción de residuos está directamente relacionada con las actividades económicas y con la demanda de materiales en la sociedad. El origen de la producción de residuos está influenciada por el consumo de recursos para la producción de materiales [2]. El aumento y los diferentes subproductos generados por distintas industrias, está asociado a problemas de gestión que conllevan un aumento de la acumulación en vertedero, debiéndose considerar los impactos que este factor causa.

Este hecho ha provocado el desarrollo de nuevas políticas medioambientales, que establecen pautas para optimizar la gestión de los mismos. Estas políticas, en términos generales, tratan de: *Minimizar* (reducción de residuos, cambiando pautas en la producción industrial), *Valorizar* (reciclaje por medio de las técnicas existentes y la reutilización directa o indirecta del material) y el *Tratamiento* (reducir la toxicidad del residuo, cuyo fin último es el vertedero).

La construcción sostenible se entiende como un concepto tiene como objetivo la generación de productos eficientes y respetuosos con el Medio Ambiente.

Según el EconomyWacht [3], la construcción civil se considera un sector muy influyente en la economía mundial. Siendo a su vez, el sector con mayor consumo de materias primas.

Además de este consumo, se debe tener en cuenta los recursos utilizados para la transformación de materias primas en subproducto, como energía y transporte que conllevan la generación de residuos [4].

Según el EconomyWacht [3], el consumo de energía en el sector de la construcción civil es de aproximadamente 2/5 partes del consumo de energía mundial.

La sostenibilidad dentro del sector de la construcción se puede alcanzar mediante estrategias de reutilización y reciclaje de los subproductos industriales y residuos de construcción. El concepto de "residuo" debería tender a desaparecer y dejar paso a la consideración de este flujo de materiales como un "recurso".

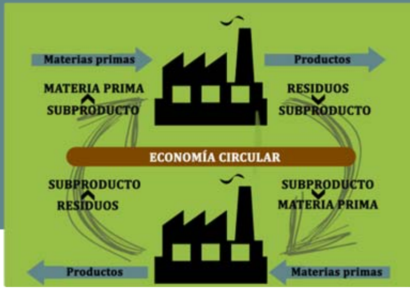
En este sentido uno de los pilares de la sostenibilidad de nuestra sociedad debe ser el uso eficiente de los recursos, el incremento del reciclado y la reutilización de los residuos, minimizando las emisiones.

Centrándonos en el foco de la industria de la construcción, la utilización de residuos y subproductos en este sector representa una vía importante de valorización [5], dado que este sector puede asumir grandes cantidades de residuos en sus fases de producción. Este reciclaje soluciona de forma conjunta la problemática de la generación de residuos destinados a vertedero y la obtención de una nueva materia prima que reduce el consumo de recursos naturales.

Sin embargo, es muy importante, informar acerca de las líneas estudiadas para la aplicación de residuos y subproductos, para gracias a su conocimiento, incentivar y promover su utilización.

En este contexto se desarrolla la presente Tesis Doctoral, la cual tiene por objeto analizar la posibilidad de utilización de diferentes subproductos generados y acumulados en grandes cantidades procedentes del sector industrial y de la construcción en la fabricación de materiales de construcción. De esta forma, se lleva a cabo una ampliación del conocimiento sobre la aplicación de RCD-ARM (Residuos de Construcción y Demolición, de forma particular se lleva a cabo el estudio de áridos reciclados mixtos) estos residuos están extensamente estudiados, pero es necesario profundizar en sus posibles aplicaciones. Además de avanzar en el estudio de aplicabilidad de este residuo, se lleva a cabo un estudio de la situación actual de generación y acumulación de subproductos industriales que lleva a desarrollar las líneas de investigación en la Presente Tesis Doctoral. Por lo que se desarrolla el estudio para potenciar la aplicación de subproductos acumulados en vertedero de tres grandes focos de producción industrial, EAI (Escorias procedentes de la producción de productos de Acero Inoxidable), CFB (Cenizas de fondo que se producen en la generación de electricidad mediante la combustión de biomasa) y por último se estudia la viabilidad de uso de FY (fosfoyeso acumulado en grandes balsas procedente de la producción de ácido fosfórico para la fabricación de fertilizantes).

1.- Subproductos y fin de condición de residuos



*El paso de **residuo a subproducto** convierte al material en materia prima para su reutilización en diversos procesos.*

En el contexto actual, la industria ha sufrido una recesión derivada del precio de la energía, la volatilidad de los costes y la falta de materias primas. Por ese motivo y todo lo expuesto anteriormente, el aprovechamiento de residuos como recursos constituye una apuesta y una oportunidad de negocio. El modelo de crecimiento basado en la secuencia lineal "*tomar-fabricar-consumir y eliminar*" pone en serios riesgos la competitividad de Europa. Por este motivo, el avance hacia una economía circular basada en el aprovechamiento de recursos y aumento del tiempo de vida útil está en auge. La consolidación de economía circular como nuevo concepto incorpora al circuito económico los residuos, convirtiéndose crucial para la industria (figura 2.1)

Figura 2.1: Economía circular [6]

Un marco jurídico sólido que sea de aplicación en toda Europa que refleje la reutilización de residuos como recurso es una herramienta clave para el tránsito a esa economía circular. Contribuyendo a la consideración de dos nuevas figuras alternativas: los subproductos y las materias primas secundarias (fin de condición de residuo).

En este contexto europeo y global, la Estrategia Española de Economía Circular queda definida en "España Circular 2030" (figura 2.2). Los ejes de actuación sobre los que se focaliza esta estrategia son: producción, consumo, gestión de residuos, materias primas secundarias, y reutilización del agua.

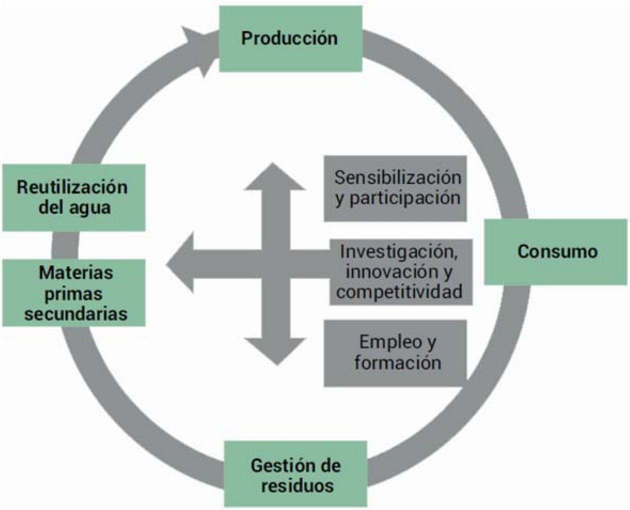


Figura 2.2: Ejes de actuación de la Estrategia Española de Economía circular

En este aspecto, se desarrolla la ley que introduce los conceptos de "*subproducto*" y de "*fin de la condición de residuo*" (figura 2.3), cuestión que abre las posibilidades para que la industria desclasifique algunos de sus residuos, siempre que se cumplan unas determinadas garantías en cuanto a posibles problemáticas ambientales y de salud, posible uso sin transformación y existencia de mercados que los demanden.

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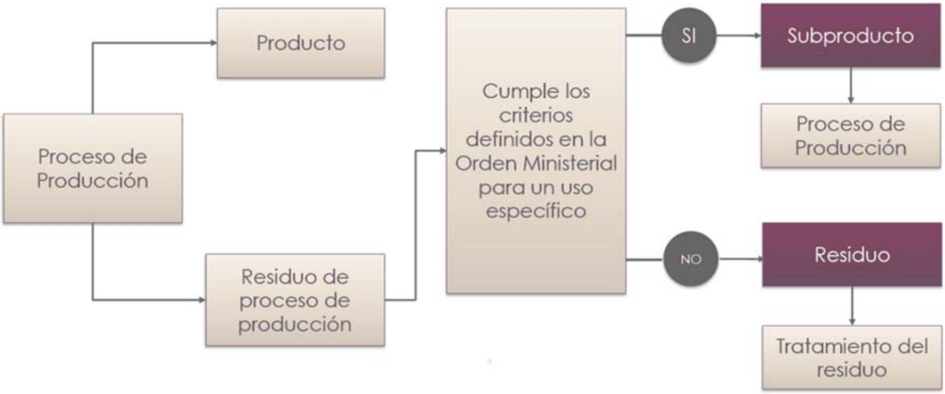

Figura 2.3: Árbol de decisiones. ¿Residuo o subproducto? [7]

Debemos conocer que establece la normativa como residuo, las bases establecidas para aplicar el fin de condición de residuo y así, cerrar el ciclo considerando el residuo como subproducto.

1.1. Concepto de residuo

El artículo 3 a) de la Ley 22/2011 de Residuos y Suelos Contaminados [8], haciéndose eco de lo dispuesto por la Directiva 2008/98/CE del Parlamento Europeo y del Consejo de 19 de noviembre de 2008 [9] sobre los residuos y por la que se derogan determinadas Directivas (en adelante la DMR) define como residuo "*cualquier sustancia u objeto que su poseedor deseche o tenga la intención o la obligación de desechar*".

La gestión de los residuos producidos, su entrega a gestor autorizado o bien, la puesta en disposición de los mismos a un agente para su posterior gestión, es responsabilidad directa del productor.

La consideración de un material como residuo, salvo excepciones, conlleva asimismo:

i. *Limitación para la comercialización y reducir el consumo del material.*

ii. *Una pérdida de valor en el mercado asociada al material debido a las limitaciones de uso.*

iii. *Obligaciones que debe asumir el productor, entre otras:*

- *La gestión (por el propio productor o por gestores autorizados) en función de la categoría que el Listado Europeo de Residuos (LER) le asigna al material.*
- *Correcto almacenamiento, mezcla, envasado y etiquetado del material en cuestión.*
- *La inscripción en el correspondiente registro de producción de residuos.*
- *La formalización de la declaración anual de residuos industriales, y la cumplimentación de las fichas de aceptación y de las hojas de seguimiento, entre otras obligaciones documentales.*
- *El cumplimiento de la normativa de traslado de residuos, ya se efectúe dicho traslado dentro del Estado o se trate de un traslado internacional.*

Por estas responsabilidades exigidas y posteriores a la legislación que promueve el fin de condición de residuos, las industrias enfatizan la catalogación de sus residuos industriales como subproductos.

1.2. Concepto de subproducto

Más allá de la distinción entre producto y residuo de producción, debemos examinar cuándo un residuo de producción es apto para abandonar la consideración de residuo y convertirse en un subproducto.

En España, la Ley de Residuos positivizó y reguló (ex art. 4) la figura del subproducto, a imagen y semejanza de cómo lo había hecho la DMR y en los siguientes términos:

“1. Una sustancia u objeto, resultante de un proceso de producción, cuya finalidad primaria no sea la producción de esa sustancia u objeto puede ser considerada como subproducto y no como residuo definido en el artículo 3, apartado a) cuando se cumplan las siguientes condiciones:

a) Que se tenga la seguridad de que la sustancia u objeto va a ser utilizado ulteriormente,

b) que la sustancia u objeto se pueda utilizar directamente sin tener que someterse a una transformación ulterior distinta de la práctica industrial habitual,

c) que la sustancia u objeto se produzca como parte integrante de un proceso de producción, y

d) que el uso ulterior cumpla todos los requisitos pertinentes relativos a los productos así como a la protección de la salud humana y del medio ambiente, sin que produzca impactos generales adversos para la salud humana o el medio ambiente”.

“2. La Comisión de coordinación en materia de residuos evaluará la consideración de estas sustancias u objetos como subproductos teniendo en cuenta lo establecido, en su caso, al respecto para el ámbito de la Unión Europea y propondrá su aprobación al Ministerio de Medio Ambiente y Medio Rural y Marino que dictará la orden ministerial correspondiente”.

La agrupación de las sustancias se realiza según tres variables, dependiendo del sector de origen, el proceso de producción que genera el residuo y el proceso productivo que lo reutiliza (figura 2.4).

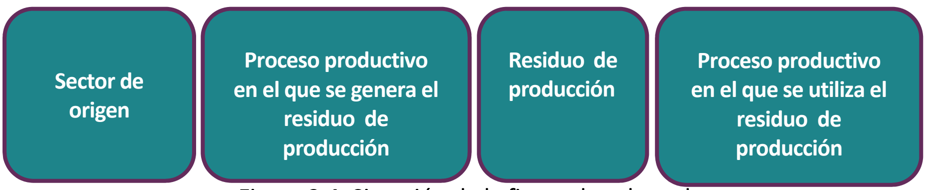

Figura 2.4: Situación de la figura de subproducto

Los principales sectores productores son: Industria de metales, de productos cerámicos, química, papelera, de los plásticos, sector de la construcción, etc.

Los principales usos como: materiales reciclados en el propio proceso de producción, como áridos en construcción, como ingredientes en la fabricación de cemento, como material de relleno, proceso de la industria química, fertilizante, etc.

Los materiales: escorias, arenas de fundición, polvo y cascarilla metálica, material cerámico, hormigón y arenas, etc.

1.2.1 Condiciones para la calificación de un material como subproducto

Garantizar la seguridad en el uso de un material es esencial para que este no sea almacenado y finalmente depositado como residuo.

El mandato del apartado 2 del artículo 4 de la Ley de Residuos en orden a instrumentar un procedimiento de declaración de subproducto, pretende uniformizar una regulación, completamente dispar en la mayoría de las Comunidades Autónomas. Con ese propósito, el Ministerio de Agricultura, Alimentación y Medio Ambiente (MAGRAMA) presenta la elaboración del procedimiento para declaración de subproducto.

El procedimiento de declaración de subproducto subdivide el trámite en dos fases diferenciadas, que se describen a continuación.

1. Valoración de la procedencia de declaración de un residuo de producción como subproducto.

- Solicitud y presentación de la información al MAGRAMA.
- Elaboración de un Informe justificativo:
    - ✓ Propiedades del material
    - ✓ Proceso en el que se utiliza el material
    - ✓ Normas
    - ✓ Sistema de Calidad
    - ✓ Destino actual
    - ✓ A que producto sustituye

- Información sobre la seguridad del material:
    - ✓ Peligrosidad de los materiales

- ✓ Cantidades
- ✓ Manipulación
- ✓ Demanda y uso del producto final

- Información sobre impacto ambiental y salud derivado el uso.

2. Comunicación específica para el uso autorizado en una instalación determinada.

1.3. Concepto de fin de la condición de residuo

De acuerdo con el primer párrafo del artículo 5 de la Ley de Residuos, la operación de valorización resulta imprescindible para que un residuo pueda perder ese estatuto jurídico.

La Guía interpretativa señala que el fin de condición de residuo se alcanza cuando se completa la operación de valorización (ya sea preparación para la reutilización, reciclaje o cualquier otro tipo de valorización). Además, debe cumplir ciertos criterios específicos:

1. Existe un uso específico para la sustancia u objeto.
2. Existe demanda en el mercado.
3. Cumple los requisitos técnicos para su uso específico y cumple la legislación existente y las normas aplicables a los productos.
4. Su uso no generará impactos adversos para el medio ambiente o la salud.

Mediante la presente Tesis Doctoral, se estudian tres importantes focos de generación de residuos que se consideran materiales potenciales para calificarlos como subproductos. Comprobando mediante los estudios desarrollados las características técnicas de los mismos y la viabilidad de uso en materiales en base cemento utilizados en el sector de la construcción.

1.4. Marco legal

La viabilidad de uso de subproductos hasta la fecha acumulados en vertedero lleva a realizar un estudio previo del marco legal existente y de las previsiones desarrolladas por los organismos competentes.

En este apartado se analiza la situación legal y la normativa que afecta a la gestión de residuos y subproductos industriales. El análisis de la situación legal pretende determinar los requerimientos de partida en la gestión de residuos.

1.4.1. Marco Legal Europeo

La Directiva marco de residuo se creó en 1975 en Europa, a partir de esa fecha, se han redactado diferentes directivas adicionales que tratan determinados flujos de residuos [9].

La aplicación de esta directiva no se ha desarrollado plenamente debido a la falta de prioridad por parte de los Estados miembros de la comunidad que consideran que no hay datos fiables sobre la calidad del material y su aplicación [10]. La aplicación de la legislación debe realizarse de formar más estricta y contar con el apoyo institucional de la UE para asegurar un desarrollo sostenible.

Además, deben ser considerados otros factores que causan daños ambientales, así como, un incremento de costes y daños a la salud humana. Debido al incumplimiento de requisitos impuestos por la UE, como es el uso inadecuado de tecnología para la gestión de los residuos en vertedero y en otras instalaciones y los traslados ilegales.

Queda expuesto a continuación una visión general de la legislación comunitaria vigentes y su estado de aplicación [10]:

Directiva marco sobre residuos (2008/98/EC)

La Comisión Europea publica en 2007 una Comunicación interpretativa sobre los residuos y subproductos, quedando definidos los términos de la siguiente forma:

- *Producto. Todo material obtenido deliberadamente en un proceso de producción. En muchos casos es posible identificar un producto "primario" (o varios), que es el principal material producido.*
- *Residuo de producción. Material que no se produce deliberadamente en un proceso de producción, pero que puede ser o no residuo.*
- *Subproducto. Residuo de producción que no es residuo.*

Un material no es calificado como residuo según el Tribunal de Justicia, si la reutilización de forma segura es posible, además de no ser necesaria una transformación previa ni una solución de continuidad en el proceso productivo [11, 12].

Posteriormente, la UE presenta la Directiva 2008/98/EC del Parlamento Europeo y del Consejo, de 19 de noviembre de 2008 [9], sobre los residuos que deroga las directivas 75/439/CEE [13], 91/689/CEE [14] y 2006/12/CE [15] basándose en la necesidad de una nueva directiva que elimine la relación ente la generación de residuos y el crecimiento económico.

Esta directica enmarca el control de los ciclos de residuos, partiendo de su producción hasta su eliminación y centrándose en la valorización y reciclaje. Su principal objetivo es la protección del medio ambiente y salud humana a través de la prevención de los efectos nocivos que genera el ciclo producción-gestión de residuos [16].

La revisión de la DMR 2008 se basa en un nuevo enfoque de la gestión de residuos centrado en la limitación del impacto sobre el medio ambiente y la salud humana. Esta gestión se centra en la implantación de una jerarquía que prioriza la prevención. Se amplía la responsabilidad del productor en relación a la generación de los mismos y fomentar el reciclado y recuperación mediante recogida selectiva.

Marco Legal en España

En España, la planificación actual de la gestión eficiente de los residuos gira en torno al Programa Estatal de Prevención de Residuos 2014-2020, al Plan Estatal Marco de Gestión de Residuos (PEMAR 2016-2022) y al Plan Nacional Integrado de Residuos para el periodo 2017-2019 (PNIR 2017-2019). Estas iniciativas están en línea con la mencionada Estrategia 2020 y con los objetivos prioritarios del VII Programa de Medio Ambiente de la UE vigente hasta 2020.

La nueva Ley 22/2011, de 28 de julio, de residuos y suelos contaminados [8] y la Ley 11/1997, de 24 de abril, de envases y residuos de envases [17], completan la normativa española en materia de residuos.

El desarrollo de esta legislación establece reglamento específicos que regulan algunos flujos de residuos. Entre ellos podemos recalcar la regulación de los Residuos de construcción y demolición (*Real Decreto 105/2008)*

Además, deben ser consideradas la Ley 16/2002 de prevención y control integral de la contaminación, el Real Decreto 653/2003 de incineración de residuos o el Real Decreto 1481/2001 de eliminación de residuos mediante depósito en vertedero. Las operaciones de valorización y eliminación de residuos están reguladas por la Orden MAM/304/2002.

A nivel autonómico, también existe legislación de carácter autonómico. En el caso de Andalucía, el Plan Director de Residuos no Peligrosos de Andalucía 2010-2019 y Plan de Gestión y Prevención de Residuos Peligrosos 2012-2020.

El desarrollo de todas estas normativas en relación a la gestión de residuos lleva a plantear el debate sobre la barrera existente entre residuos y materias primas. ¿Cuándo un residuo deja de serlo? o ¿es materia prima secundaria o residuo?

1.5. Generación y gestión de residuos y subproductos industriales

En toda Europa, por tanto, también en España, la generación de residuos se relaciona de forma directa con el crecimiento demográfico. En 2014 según Eurostat se generaron en España 38,7 millones de toneladas de residuos, un 9,4% menos que en 2012. El 96,6% de estos residuos fueron no peligrosos [18].

Casi el 50% de los residuos se generaron en la construcción y la industria (figura 2.5).

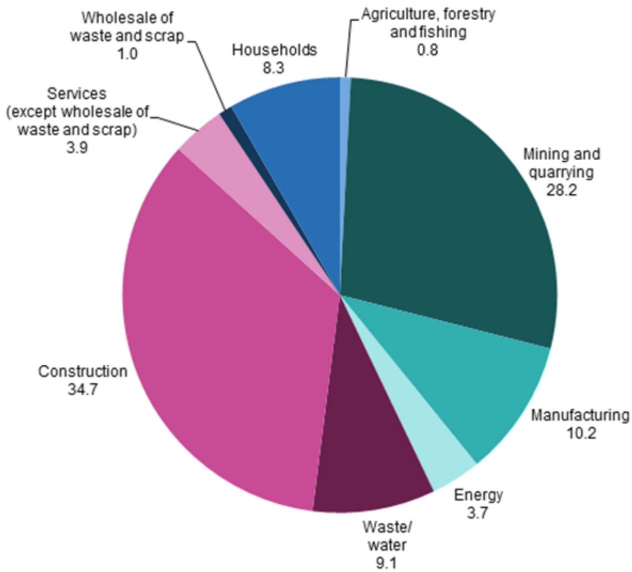

Figura 2.5: Generación de residuos por actividades económicas y hogares, EU-28, 2014. [19]

En cuanto al tratamiento y según Eurostat, en 2014. Aunque se han conseguido avances en la reutilización de residuos en los últimos años, el 55% del total se transportaban a vertedero [18]. Debe ser modificada la situación actual en relación al tratamiento de residuos (figura 2.6).

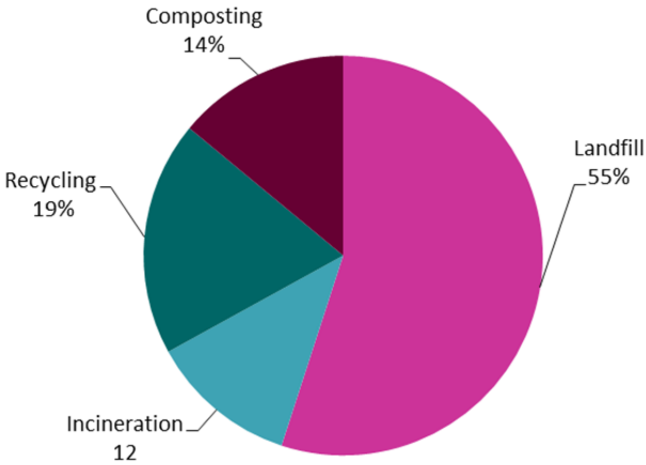

Figura 2.6: Tratamiento de residuos, España, 2014. [19]

A la situación negativa actual en la gestión y tratamiento de los residuos se suma la demanda de materias primas en la producción industrial (figura 2.7):

1. A medida que la sociedad crece, el uso de las materias primas se incrementa.
2. Por otra parte, este elevado consumo de recursos no renovables lleva a una disminución progresiva de las reservas. Este hecho incentiva de cierta forma la necesidad de convertir residuos no deseados en materias primas utilizables.

Por otra parte ambos aspectos se reflejan en impactos de gran calado.

3. Como son las modificaciones provocadas en el entorno debido a la extracción de las materias primas, emisiones debidas al trasporte, consumo energético, etc.
4. La retirada del residuo, requiere a su vez una nueva ocupación del suelo, generalmente de temporalidad indefinida y en ubicaciones distintas de la de extracción, mayor carga de consumo energético para su transformación y transporte, etc.

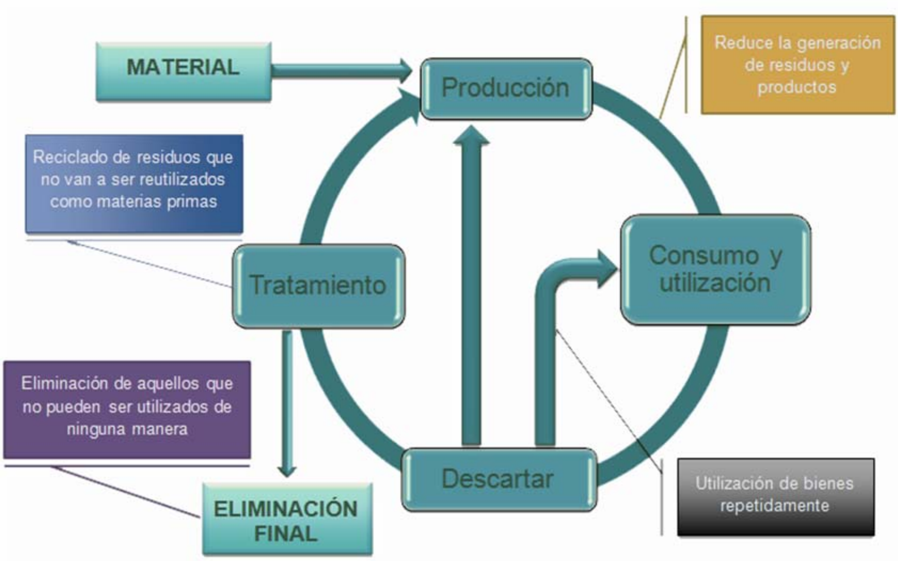

Figura 2.7: Ciclo de Producción de Residuos [20]

2.- Evaluación del impacto ambiental y construcción sostenible

La reutilización de ***subproductos*** *en un segundo ciclo de vida está marcado por su* ***viabilidad técnica*** *y por el* ***impacto ambiental****.*

La economía circular está sustentada por un pilar fundamental como es la protección del medio ambiente y garantizar la salud de las personas mediante la introducción de materias primas secundarias.

La idea de la sostenibilidad resurgió en 2011 con la Ley de Economía Sostenible [8]. La ley definía concretamente la economía sostenible como aquella que reconcilia el desarrollo económico, medioambiental y social.

La convocatoria específica “Industria 2020 en la Economía Circular” ha invertido en la demostración de la viabilidad ambiental, social y económica. Este enfoque se mantiene en el periodo 2018-2020 centrándose en actividades de innovación e investigación en el sector industrial para llegar al sistema de Economía Circular. El gasto total del gobierno en protección del medio ambiente aumentó alrededor del 76% en valor real entre 2000 y 2010, a pesar de la crisis económica (figura 2.8).

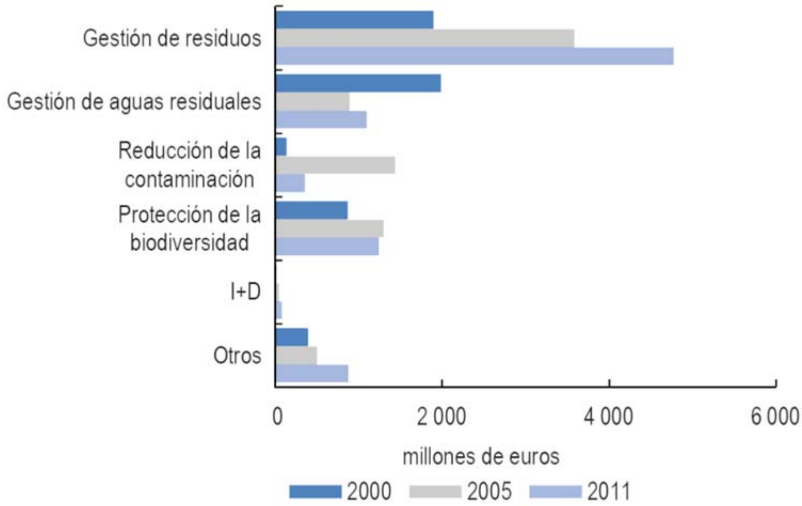

Figura 2.8: Gasto público medioambiental dentro de la industria. [21]

Podemos observar el incremento en la inversión económica en la gestión de residuos del sector industrial.

Dentro de esa inversión en la gestión de residuos industriales se considera el impacto ambiental que ocasiona la reutilización de subproductos industriales en nuevos materiales de construcción sostenible. Por este motivo, se plantea la incógnita sobre si su uso puede causar impacto negativo en el medio al ser reutilizado en nuevos materiales de construcción o si por el contrario, la afección que sobre ellos causan los agentes externos, en concreto el agua de lluvia, pueden dar lugar a fenómenos de lixiviación y percolación de elementos tóxicos presentes en dichos subproductos, lo cual podría causar la contaminación de aguas superficiales y subterráneas [22].

Por lo tanto, la presente Tesis Doctoral aborda aspectos ambientales que deben ser considerados para la aplicación de subproductos en el ámbito de la construcción. Partimos de la base de que estos subproductos pueden contener elementos tóxicos solubles que pueden dar lugar a la liberación de metales pesados, sulfatos, cloruros y compuestos orgánicos, ya que cuando el agua entra en contacto con ellos, se producen procesos de lixiviación produciendo una amenaza para el medioambiente.

El fenómeno de lixiviación está afectado por varios factores físicos, como el tamaño de partículas expuestas, tiempo, condiciones de flujo lixiviante, temperatura, porosidad, forma geométrica y tamaño de los materiales, permeabilidad de la matriz, condiciones hidrogeológicas, etc. Así como una serie de factores químicos: pH del material, equilibrio o control cinético de la liberación, formación de complejos inorgánicos u orgánicos, condiciones redox del material, etc. Además, en términos de comportamiento frente a la lixiviación, se debe distinguir según el tipo de material y/o de infraestructura de la cual formará parte: materiales monolíticos (materiales base cemento, hormigón, ladrillos, materiales recubiertos, etc.) y materiales granulares (áridos, cenizas, escorias, etc.). En los materiales monolíticos la lixiviación está controlada por difusión, mientras que en los materiales granulares, la liberación está dominada por mecanismos de percolación [22]. Todos estos factores quedan mostrados en la siguiente figura (figura 2.9 y figura 2.10).

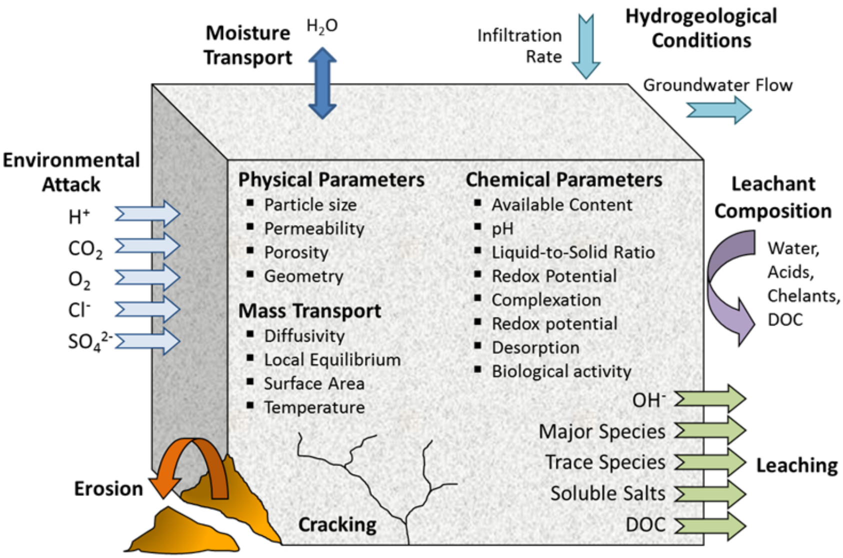

Figura 2.9: Factores externos (químicos y físicos) que influyen en la liberación de contaminantes en materiales monolíticos (hormigón, bloques, ladrillos, etc.)

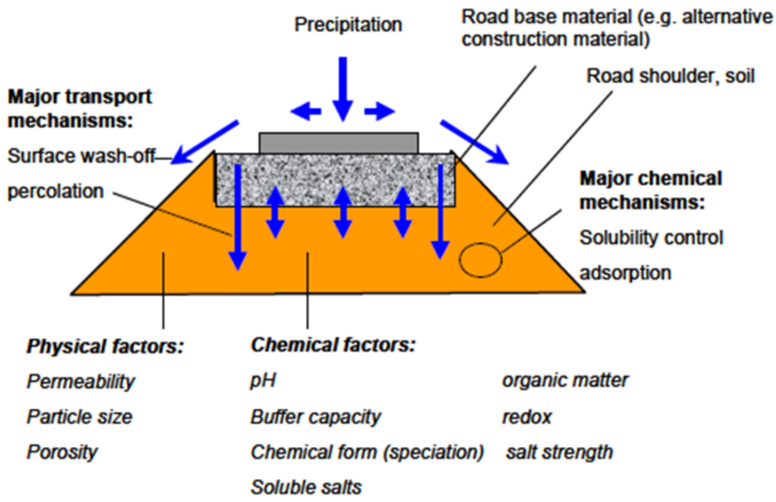

Figura 2.10: Factores externos (químicos y físicos) que influyen en la liberación de contaminantes en materiales de material granular (arena, grava, ceniza, escoria de acero, etc.), tal y como se aplica formando parte de la infraestructura de una carretera.

Los ensayos de lixiviación son los más indicados para reproducir en laboratorio los procesos físico-químicos que tienen lugar bajo las condiciones de exposición que los materiales en base cemento fabricados con subproductos tendrán en condiciones reales [23]. Se pueden distinguir los siguientes tipos de ensayos de lixiviación:

- Test de conformidad: consiste en un test de lixiviación básico y rápido de una o dos etapas en el cual el material se encuentra en estado granular (p.e. UNE EN 12.457-3). El material se pone en contacto con agua y se somete a agitación mecánica, realizándolo para dos relaciones de líquido/sólido (2 y 10 L/kg) y expresando la liberación en (mg/kg de materia seca).
- Test de Columna o de percolación: consiste en un test de lixiviación también para materiales granulares con la diferencia que en este caso el ensayo tiene capacidad de analizar el comportamiento a largo plazo (con 7 relaciones liquido/sólido (L/S):0.1, 0.2, 0.5, 1, 2, 5, y 10 L/kg).

Este ensayo simula en laboratorio el mecanismo de percolación que dicta la liberación de elementos químicos (expresados en mg/l) en cualquier material granular puesto en obra, ya que depositando el material en el interior de columnas se hace circular un flujo ascendente de agua a través de la misma, simulando la circulación del agua de lluvia (p.e. NEN 7343:2004).

- Test de Tanque o de difusión: consiste en un test de lixiviación para materiales monolíticos. Consiste en reproducir en el laboratorio el mecanismo de liberación que rige la liberación en materiales sólidos: la difusión superficial de especies químicas expresada en mg/kg (NF X31-211).

Por este motivo, un completo estudio del proceso de lixiviación y de liberación de contaminantes, permite utilizar los resultados como indicadores de sostenibilidad, necesarios para dejar patente la idoneidad de poder reutilizar subproductos industriales en ingeniería civil y es por este motivo que la presente Tesis Doctoral ha incluido los ensayos de lixiviación de Test de Conformidad y Test de difusión de apoyo en las investigaciones realizadas, siendo sus resultados determinantes en la decisión de utilización o no de dichos materiales.

Debido a la multitud de factores que influyen en el proceso de lixiviación se considera esencial la elección del tipo de test, ya que al omitir estos factores, se corre el riesgo de obtener resultados no extrapolables a situaciones reales. Por todo ello, es esencial definir el escenario de lixiviación.

Hay que tener en cuenta que las pruebas de lixiviación se llevan a cabo para una amplia variedad de materiales ya que son necesarias para diferentes fines: regulación, gestión de residuos, evaluación de impacto ambiental o fines científicos. Debido a la creciente preocupación por el impacto que la actuación humana pueda tener en el medio ambiente, las pruebas de lixiviación están cada vez más implantadas en el sistema de gestión de cualquier residuo y subproducto. Y es necesario destacar que hace años que investigadores comprobaron cómo hay ciertas similitudes en el comportamiento frente a lixiviación de los materiales, a pesar de tener diferentes naturaleza o composición [24].

Este autor comprobó que una sola prueba será insuficiente para cubrir toda la gama de propiedades ambientales de un material. Como hemos indicado, la lixiviación de contaminantes está controlado por un número limitado de parámetros (por ejemplo, pH, potencial redox, complejación, etc) pero que en función de un material u otro, un parámetro podrá ser más o menos condicionante en el proceso de liberación, existiendo un patrón similar. Todo ello, facilita la evaluación de materiales secundarios o subproductos.

Por tanto, el procedimiento de evaluación ambiental de cualquier subproducto que va a ser utilizado en el ámbito de la construcción sostenible, se puede resumir en el siguiente ciclo de 5 fases (figura 2.11).

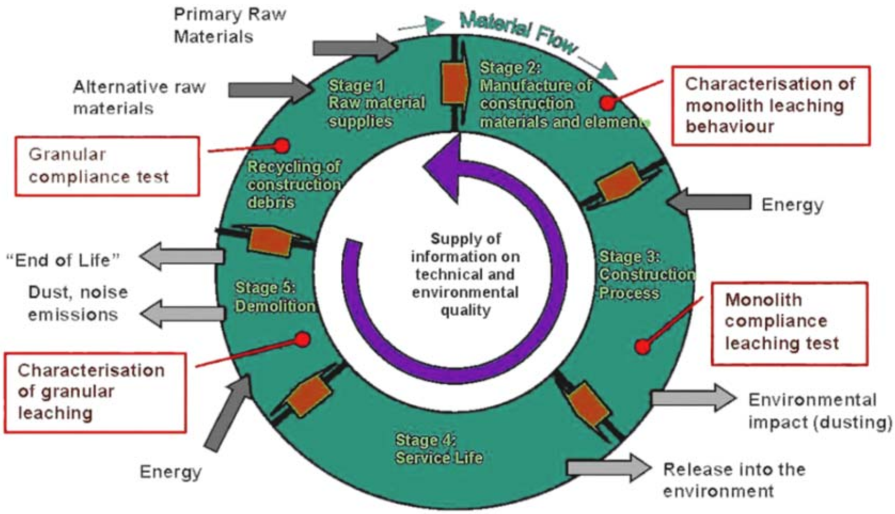

Figura 2.11: Caracterización y tests de lixiviación en diferentes etapas de suministro en el ciclo de edificación. [25]

2.1. Marco legal

La Decisión del Consejo Europeo [26], de 19 de diciembre de 2002, por la que se establecen los criterios y procedimientos de admisión de residuos en los vertederos con arreglo al artículo 16 y al anexo II de la Directiva 1999/31/CEE, se distinguen tres tipos de vertederos: vertederos para residuos inertes, para no peligrosos y para residuos peligrosos.

Para la admisión de residuos en los vertederos hay que realizar una primera caracterización básica sobre el residuo (liberación de elementos peligrosos al lixiviado). La concentración de las especies químicas críticas desde un punto de vista ambiental, se miden sobre el lixiviado obtenido mediante una prueba o **test de conformidad**. En base a los resultados obtenidos por dicho ensayo, se obtendrá el nivel de liberación del material y por tanto, se determinará la clase de vertedero en el que el residuo se considera admisible.

En cuanto a las especies químicas reguladas por la normativa vigente por ser considerados potencialmente peligrosos para el medio ambiente, son las siguientes: As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn, sulfatos, cloruros y fluoruros. Así pues, dicha normativa indica la concentración máxima (expresada en mg/kg) de cada uno de esos elementos, para cada uno de los tres tipos de vertederos: los de residuos inertes, los de no peligrosos y los de peligrosos. Estos niveles se calcularán, en términos de liberación total, para las proporciones entre líquido y sólido (L/S) de 2 l/kg y de 10 l/kg y una vez medidos los niveles liberados en el lixiviado de cada material, se compararán con los valores límite de concentración que se indican en las Tablas 2.1 y 2.2 para poder clasificar el material según su potencial contaminante.

Tabla 2.1: Clasificación de peligrosidad de residuos en función de la cantidad lixiviada (para L/S=2 l/Kg) para admisión en vertedero

Componentes	**Valores admisibles de la Directiva para una relación L/S de 2 L/kg para el Test de Conformidad para materiales granulares** *Niveles liberados por elemento (mg/kg)*		
	Residuo Inerte	**Residuo No Peligro**	**Resido Peligroso**
As	0.1	0.4	6
Ba	7	30	100
Cd	0.03	0.6	3
Cr	0.2	4	25
Cu	0.9	25	50
Hg	0.003	0.05	0.5
Mo	0.3	5	20
Ni	0.2	5	20
Pb	0.2	5	20
Sb	0.02	0.2	2
Se	0.06	0.3	4
Zn	2	25	90
Cloruro	550	10000	17000
Fluoruro	4	60	200
Sulfato	560	10000	25000

Tabla 2.2: Clasificación de peligrosidad de residuos en función de la cantidad lixiviada (para L/S=10 l/Kg) para admisión en vertedero

Componentes	**Valores admisibles de la Directiva para una relación L/S de 10 L/kg para el Test de Conformidad para materiales granulares** *Niveles liberados por elemento (mg/kg)*		
	Residuo Inerte	**Residuo No Peligro**	**Resido Peligroso**
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr	0.5	10	70
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
Cloruro	800	15000	25000
Fluoruro	10	150	500
Sulfato	1000	20000	50000

Ante la carencia de normativa y procedimiento de evaluación ambiental a nivel nacional, se recurran a las metodologías aprobadas por la Comisión Europea (v.g. test de cumplimiento UNE-EN 12457-3)

A nivel europeo, se han creado 40 comités técnicos de materiales de construcción, donde cada uno de ellos ha desarrollado su propio ensayo de lixiviación. Por ejemplo, la normativa holandesa (Dutch Building Materials Decree 1995) regula la utilización de materiales de construcción indicando valores límites particularizados para este tipo de material. Otros países como Alemania, Francia o Suiza también disponen de procedimientos propios para la evaluación de la lixiviación particularizados para residuos concretos como son tratamientos de aguas residuales o residuos sólidos municipales.

Por tanto, el objetivo fundamental de la presente Tesis Doctoral es analizar la viabilidad del uso y aplicaciones de diferentes subproductos industriales en materiales en base cemento para su uso en construcción e ingeniería civil. Es necesario considerar no sólo su comportamiento físico-mecánico, sino también la repercusión ambiental derivada de la puesta en obra de ese material.

3.- Residuos de construcción y demolición

Para la reutilización de los RCD es necesario profundizar en estudios que demuestren su viabilidad de uso en diferentes aplicaciones.

- *OBJETIVOS DE REUTILIZACIÓN*
- *RCD MAYORITARIAMENTE GENERADO (ARM)*
- *INCENTIVAR VALORIZACIÓN*

Se define como residuo de construcción y demolición (RCD) como "*cualquier sustancia u objeto que, cumpliendo con la definición de residuo del artículo 3.a) de la Ley 10/1998, de 21 de abril, se genera en una obra de excavación, nueva construcción, reparación, remodelación, rehabilitación y demolición, incluyendo el de obra menor y reparación domiciliaria*", hoy derogada por la Ley 22/2011, que "*se genere en una obra de construcción o demolición*". La gestión y producción de estos residuos queda regulada por una legislación específica [27] que tiene por objeto establecer el régimen jurídico para fomentar la reutilización, reciclado y valorización contribuyendo al desarrollo sostenible en el sector de la construcción.

Por obras de construcción y demolición se entienden [18]: aquellas actividades de reparación, reforma, nueva construcción o demolición de una construcción.

Las cantidades de RCD deben ser reducidas y es necesario centrarse en una correcta gestión que potencie su aprovechamiento como material secundario.

La composición de los RCD es muy variada, presentando productos cerámicos, residuos de hormigón, material asfáltico y en menor medida otros componentes como madera, vidrio, plásticos, etc. Esta composición RCD varía en función a su procedencia, al tipo de materias primas utilizadas y a los hábitos constructivos.

Por otro lado, el tipo de materiales utilizados en las edificaciones varía a lo largo del tiempo y con ello también cambia la composición de los RCD.

La composición media de estos residuos se refleja en la Figura 2.13.

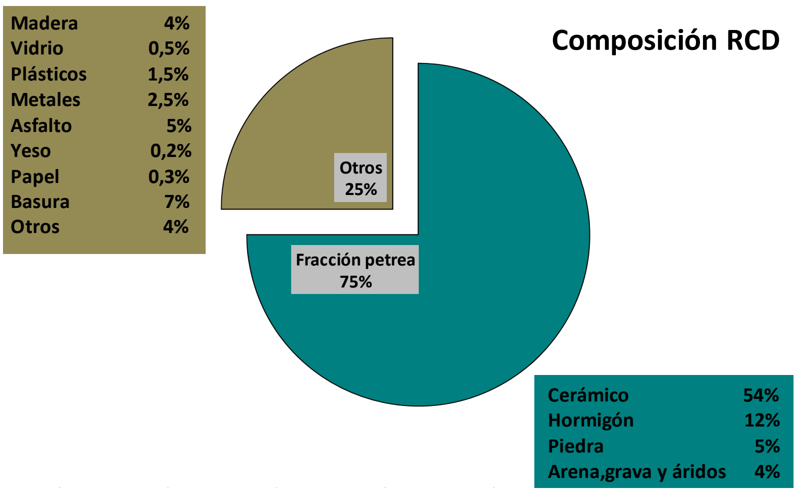

Figura 2.12: Composición Residuos de Construcción y Demolición. [28]

Como se puede observar, los RCD están compuestos mayoritariamente por materiales cerámicos y de hormigón [29]. Estos escombros mixtos o cerámicos tienen dos orígenes: los producidos en demoliciones de edificaciones. En España la mayor parte de los residuos de demolición lo forman este tipo de residuos (constituyen el 80%). Y en menor medida, ladrillos rechazados en su fabricación por no cumplir las especificaciones pertinentes (constituyen 5-10%). En este caso se trata de materiales muy homogéneos.

Respecto a los RCD de hormigón, proceden mayoritariamente de las demoliciones en obra civil.

Analizando la distribución las 67 plantas de reciclaje en España y su producción, podemos observar que los volúmenes de árido reciclado mixto son superiores a los de hormigón. El 54% de las plantas producen árido mixto, el 31% ambos tipos de áridos y únicamente el 15% producen áridos reciclados de hormigón.

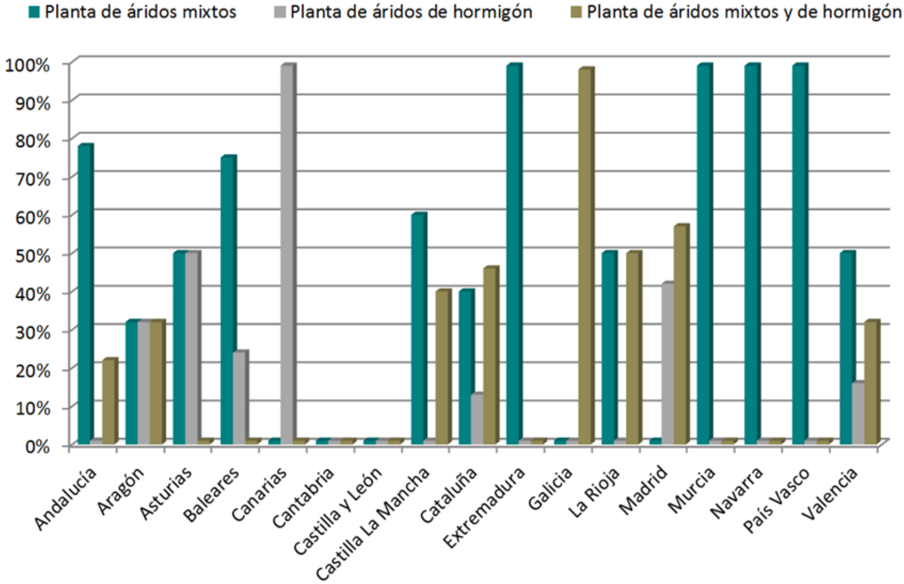

Figura 2.13: Porcentaje de plantas de reciclaje por tipo de árido producido [30].

Analizando la producción de áridos reciclados y observando que la mayor parte son residuos mixtos, además de tener en cuenta la dificultad técnica para la separación de residuos de hormigón y residuos cerámicos. Debe profundizarse en el estudio de valorización, reutilización y optimación del árido reciclado mixto. Por ese motivo, la presente Tesis Doctoral se centra en la ampliación del conocimiento sobre la aplicación de los áridos reciclados mixtos.

3.1. Áridos reciclados

El árido reciclado procede de residuos inorgánicos del sector constructivo. La procedencia de los RCD son dos: los residuos generados en el proceso constructivo y los producidos en la demolición.

Los RCD se clasifican a la salida de la planta de tratamiento en diferentes áridos reciclados, dependiendo de las proporciones de sus componentes. Áridos reciclados procedentes de hormigón, áridos reciclados procedentes de residuos cerámicos, áridos reciclados mixtos procedentes de residuos de naturaleza diversa y áridos procedentes de residuos asfálticos [31, 32]. Sus propiedades han sido ampliamente estudiadas y a día de hoy se tiene una visión general de las características de cada tipo de árido que lleva a optimizar su uso y valorización en la elaboración de diferentes materiales.

Los áridos de hormigón, mixtos y cerámicos se clasifican según diferentes propiedades, como el porcentaje en peso de partículas cerámicas, densidad y absorción de agua. Las características de los áridos dependen principalmente del tipo de material del que procedan, de los equipos de machaqueo en la planta de tratamiento, proceso de eliminación de impurezas, etc [33].

Tabla 2.3: Rango de densidad y absorción de agua para diferentes tipos de áridos reciclados. [33].

	Part. Cerámica (%)	Part. Hormigón (%)	Densidad (kg/dm^3)	Abs. Agua 24h (%)
HORMIGÓN	≤ 10	≥ 90	2.34 – 2.47	3.6 – 7.3
MIXTO	≤ 10	≥ 90	2.22 – 2.58	2.1 – 8.79
CERÁMICO	> 30	< 70	2.06 – 2.39	7.21 – 14.36

- **Áridos Reciclados de Hormigón**

Estos áridos son el resultado del proceso de machaqueo, cribado y procesamiento de los residuos de hormigón. Su contenido de partículas de hormigón es superior al 90% como se ha mostrado en la tabla 1.3.

Figura 2.14: Áridos reciclados de hormigón

Es el único tipo de árido reciclado que puede ser admisible para hormigón estructural, según la EHE-08. Para su uso, no debe contener partículas asfálticas y el contenido de impurezas debe estar dentro de unos límites, además se limita el porcentaje de sustitución del árido convencional a 20% [34], demostrándose que las propiedades mecánicas permanecen prácticamente constantes. Cuando se empleen porcentajes mayores de sustitución los efectos sobre las mismas pueden representar una limitación en distintos casos.

Las propiedades que presentan este tipo de áridos es un porcentaje menor de lajas que los áridos convencionales, una densidad menor entre un 5%-10% y como propiedad que más difiere respecto a los áridos convencionales es la absorción, con valores mostrados en la tabla 1.3. Además, el desgaste de Los Ángeles es mayor en áridos reciclados que en áridos naturales, entre 25% y 45%.

- **Áridos Reciclados Cerámicos**

Estos áridos son el producto de procesar residuos con presencia predominante de material cerámico. Se clasifican como tales aquellos áridos con un contenido de hormigón inferior al 70% y con una cantidad de partículas cerámicas superior al 20% (tabla 1.3). La principal propiedad que los caracteriza es una mayor absorción (entre un 6%-25% superior al árido convencional) y menor densidad respecto al resto de áridos reciclados [33]. Las propiedades de estos residuos pueden variar según su composición, presentando un coeficiente de Los Ángeles que disminuye a medida que aumenta el porcentaje de material cerámico situándose en valores entre 25%-50% en cuanto a sus propiedades químicas se puede estacar que puede contener sulfatos debido a la presencia de morteros, yesos, etc.

Figura 2.15: Áridos reciclados cerámicos

- **Áridos Reciclados Mixto**

Debido a que presentan el mayor porcentaje dentro de las plantas de tratamiento en España, estos áridos son el objeto de estudio de la presente Tesis Doctoral. Son el resultado del tratamiento de RCD con diferentes naturalezas, se caracterizan por un contenido de partículas cerámicas inferior al 20% y de hormigón entre el 70%-90% (tabla 1.3). Entre las propiedades identificativas de este tipo de áridos se encuentra una gran variabilidad de porcentaje de finos, entre 0,5% y 18% y una mayor absorción que el árido natural presentando valores entre un 12%-20% superiores. El coeficiente de los Ángeles se sitúa entre 28% y 47%.

Figura 2.16: Áridos reciclados mixto

3.2. Gestión de los residuos de construcción y demolición

El Real Decreto 105/2008, de 1 de febrero, por el que se regula la producción y gestión de residuos de construcción y demolición, junto con distintas iniciativas legales emprendidas en distintas Comunidades Autónomas, constituyen el cuerpo básico de herramientas que la Administración pretende implantar en el sector de la construcción con objeto de dar desarrollo a los objetivos contenidos en el Plan Estatal Marco de Gestión de Residuos.

Esta legislación manifiesta las nuevas tendencias en la gestión de residuos con mayor respeto al Medio Ambiente y optimización de recursos y materiales.

Actualmente la gestión y los objetivos de valorización y reutilización de los RCD quedan fijados en el PEMAR 2016-2022. Se establecen los siguientes objetivos cualitativos para aumentar la calidad del producto final mediante una correcta gestión.

- Establecer recogida de forma separada de los distintos materiales generados en obra y asegurar la correcta gestión.
- Fomento de la utilización de RCD mediante la implantación de medidas como la subida de tasa de vertido o establecer obligaciones

al promotor o constructor por la incorrecta separación de RCD.

- Fomentar la valorización.
- Establecer un Acuerdo Marco Sectorial para impulsar la utilización de áridos reciclados procedentes de RCD en obras de construcción. Así se propone la inclusión, siempre que sea posible, en los proyectos de construcción de obra pública de un porcentaje mínimo del 5 % de áridos reciclados. Igualmente se aplicará este porcentaje del 5 %, siempre que sea posible, en la obra privada.

Para la consecución de estos objetivos cualitativos el PEMAR establece los siguientes objetivos cuantitativos (tabla 2.4) específicos sobre RCD para los años 2016, 2018 y 2020, orientados al cumplimiento del objetivo final previsto en la Directiva Marco de Residuos para este flujo de residuos.

Tabla 2.4: Objetivos RCD para años 2016, 2018 y 2020. [18]

	2016	2018	2020
% RCD no peligrosos destinados a la preparación para la reutilización, el reciclado y otras operaciones de valorización (con exclusión de las tierras y piedras limpias) (mínimo)	60	65	70
Eliminación de RCD no peligrosos en vertedero (en %) (máximo)	40	35	30
% de tierras y piedras limpias (LER 17 05 04) utilizadas en obras de tierra y en obras de restauración, acondicionamiento o relleno (mínimo)	75	85	90
Eliminación de tierras y piedras limpias (LER 17 05 04) en vertedero (en %) respecto del volumen total de materiales naturales excavados. (máximo)	25	15	10

Como se ha indicado anteriormente, La Directiva Europea de Residuos y el Programa Marco de Residuos PEMAR, prevén que en año 2020 un 70% de los RCD deben valorizarse correctamente.

La Valorización de RCD contempla dos importantes consideraciones:

- La valorización de RCD no es la contabilización de las entradas de RCD a Gestores Autorizados, hay que conocer cuántos de estos residuos se reciclan y cuantos son finalmente eliminados en vertedero como rechazos.
- La valorización de RCD en rellenos y restauraciones debe realizarse con materiales reciclados procedentes de gestores autorizados, nunca con RCD, (las tierras limpias de excavación para rellenos y restauraciones no están contempladas).

El informe refleja que en el periodo 2011-2015 la Valorización media realizada a los RCD fue del 39%, lo que supone que todavía debemos valorizar el 31% de los RCD que producimos antes del año 2020. Mediante el desarrollo de nuevas investigaciones y basándose en resultados obtenidos de las previas se debe crear una visión de seguridad en el usuario, reflejando la características de los RCD que hacen posible su aplicación en nuevos materiales de construcción y de esta forma fomentar la aplicabilidad de los RCD para poder llegar a los objetivos fijados en 2020.

3.3. Aplicación de los áridos reciclados mixtos

Figura 2.17: Aplicaciones de ARM según Catálogo de Residuos utilizables en construcción. [35]

Desde el año 2014, los ARM están dentro del catálogo de residuos utilizables en construcción.

El avance en las investigaciones desarrolladas en las últimas décadas [36] ha llevado a una mayor utilización de áridos procedentes de RCD. Debido a que los áridos reciclados mixtos (ARM) son el producto resultante más abundante del tratamiento de los RCD, esta Tesis Doctoral se centra en la ampliación del conocimiento para su reutilización y mayor aplicación.

Los estudios mostrados por diferentes autores [33, 37, 38] coinciden en que las propiedades de los ARM presentan mayor variabilidad, muestran una menor densidad, mayor absorción y propiedades físicas inferiores que los áridos naturales, así como un mayor desgaste. Estos motivos hacen que pese a las elevadas tasas de generación de ARM la expansión en su aplicación represente un obstáculo.

En la actualidad, la mayor parte de los ARM se utilizan en obras que no presenten altas exigencias técnicas [39]; entre ellas se encuentran las siguientes aplicaciones:

- **<u>Bases y sub-bases de carreteras</u>**. Podemos clasificar estas aplicaciones en dos tipos:

i. ARM como material no ligado. Según el artículo *510 del PG-3*, se define zahorra como aquel *"material granular, de granulometría continua, utilizado como capa de firme*", siendo la zahorra natural aquella formada por partículas no trituradas y la zahorra artificial la formada por partículas total o parcialmente trituradas. Jiménez et al. [40] evaluaron el comportamiento de los ARM aplicados en explanadas y capas estructurales de carreteras rurales, obteniendo resultados altos de capacidad de soporte (según el ensayo CBR), resultados similares fueron obtenidos por Poon y Chan [41]. Mostrando que las principales propiedades limitantes para el uso de ARM es el contenido en sales solubles y yeso y menor resistencia a la fragmentación.

Vegas et al. [42] exponen en su estudio pre-normativo la viabilidad de uso de ARM limitando el contenido de material cerámico por debajo del 35%, el contenido de materia orgánica por debajo de 0,8%, y el contenido de sulfatos solubles por debajo de 0,4%. Constituyendo un material granular que es técnicamente viable para su uso en capas estructurales no consolidadas de carreteras. Al igual que Sherwood [43] propuso en su estudio en el que exponía que una reducción de los requisitos establecidos en las normativas nacionales llevaría a un aumento del uso de materiales secundarios. Por ese motivo, el incumplimiento de los áridos reciclados mixtos del coeficiente de Los Ángeles y contenido de azufre total no limitaría su uso como sub-base en caminos rurales.

Los resultados obtenidos en laboratorio han sido corroborados en aplicaciones en tramos reales. Existen secciones experimentales de tramos de carreteras en España construidas con ARM en los últimos años. Jiménez et al. [40] ponen de manifiesto su viabilidad de uso en caminos rurales, obteniendo valores mayores de sales solubles que los establecidos en el PG-3. Se comprueba que el contenido de sales solubles puede elevarse hasta 1,3% sin reducir la calidad de los caminos rurales. Así como, fueron aplicados ARM en la Ronda de Circunvalación Oeste de Málaga [44]. Donde fueron aplicados ARM en capas de suelo cemento, con resultados muy positivos.

ii. ARM como material tratado con cemento. Según artículo 513 del PG-3, se define material tratado con cemento como *"la mezcla homogénea, en las proporciones adecuadas, de material granular, cemento, agua y eventualmente aditivos, realizada en central, que, convenientemente compactada, se utiliza como capa estructural en firmes de carretera".*

Se ha comprobado que el tratamiento de áridos reciclados con cemento, reduce la susceptibilidad frente a hielo, permeabilidad y lixiviación [45].

El comportamiento de ARM estabilizado con cemento para su aplicación en bases y sub-bases de carreteras ha sido estudiado por diversos autores [44, 46]. Estos estudios demuestran en pruebas piloto la capacidad cementante remanente que presentan estos áridos, teniendo en consideración que el contenido de sulfatos debe ser limitado [47].

- <u>Hormigón</u>. Las propiedades finales adquiridas definen el uso de ARM en dos tipos de hormigones:

i. ARM en hormigones no estructurales. El amplio conocimiento sobre la aplicación de áridos reciclados de hormigón en la fabricación de hormigón ha llevado a diversos autores a evaluar el uso de ARM en la fabricación de hormigón no estructural [33, 48-50]. De acuerdo con la normativa vigente, en el anejo 18 de la EHE-08 se define hormigón de uso no estructural, aquellos que no comprometen estructuralmente la construcción pero que desempeñan una función de mejora de las condiciones de durabilidad. En la fabricación del hormigón no estructural es posible el empleo del 100% de árido grueso reciclado.

Estos áridos deben cumplir las especificaciones definidas en el Anejo nº 15 de esta Instrucción.

Al igual que ocurre en la posibilidad de aplicación de ARM, los estudios realizados muestran que la limitación más restrictiva que debe cumplir el uso de ARM en hormigón no estructural es el contenido total de sulfatos [48]. Esta razón es considerada por diversos autores la principal que limita la cantidad de árido mixto como sustituto de áridos convencionales en la dosificación de hormigón. En esta línea, Poon y Chan [51] indican que el uso de áridos finos de ladrillos y ladrillo triturado con un reemplazo del 20% de arena natural es adecuado para todas las aplicaciones de hormigón. La aplicación de ARM en hormigón no estructural se ha basado en investigaciones sobre hormigón en masa para relleno y hormigones para acerados y bordillos [52-54].

ii. ARM en hormigones estructurales. Según EHE-08, limita al árido de hormigón como el único admisible para ser utilizado en hormigón estructural, imponiendo valores límites de impurezas que pueden afectar a la durabilidad y resistencia. El resto de áridos reciclados pueden ser usados en aplicaciones de menor exigencia. La composición química de los ARM, según Martín-Morales et al. [39] es su punto más desfavorable, mayoritariamente por los valores altos de sulfatos y cloruros. En el estudio llevado a cabo por Khalaf y DeVenny [55], afirman que siempre que las impurezas de los áridos reciclados cerámicos estén dentro de los límites establecidos por normativas internacionales y nacionales es posible el diseño de dosificaciones para el hormigón que incluyan estos áridos como sustituto del árido grueso convencional.

Por tanto, estas propiedades químicas y físicas de los ARM llevan a limitar su utilización en la fabricación de hormigón estructural, debido a que el uso de la fracción gruesa de ARM lleva a una disminución de la resistencia a compresión a medida que aumenta la tasa de aplicación. Debido a la reducción de las propiedades mecánicas, la mayoría de los estudios recomiendan una tasa de sustitución por áridos naturales entre el 20-50% [49, 56, 57]. Además, ha sido demostrada que el uso de ARM resulta en un hormigón con menor densidad y mayor absorción, además de una reducción de las propiedades de durabilidad. Pero el estudio de una dosificación y nivel de reemplazo adecuado permite su uso obteniendo un hormigón con características adecuadas.

- **Morteros.** La elaboración de morteros de albañilería supone una alternativa para la utilización de la fracción fina de los ARM. Una sustitución muy alta de arena natural por árido reciclado conllevaría el encarecimiento del mortero por la necesidad de una sobredosificación de cemento para llegar a las resistencias mínimas exigidas [39]. La mayoría de los estudiados se han basado en la aplicación de áridos reciclados de hormigón. Aspectos a considerar son la excelente adherencia obtenida en morteros fabricados con ARM [58] aunque las propiedades mecánicas se vieron afectadas. Para un 15% de sustitución de arena natural por la fracción fina de ARM, las propiedades mecánicas no se vieron afectadas [59]. Debido a la baja densidad de este material, autores han desarrollado sustituciones volumétricas para la fabricación de morteros [60] demostrando que con sustituciones del 20% se consiguieron mejoras en el comportamiento mecánico y propiedades de durabilidad presentando como característica negativa su mayor retracción.

Analizando todas las investigaciones previas de viabilidad de aplicación de ARM llevan a desarrollar una ampliación del estudio de los ARM considerando principalmente sus propiedades físicas de baja densidad para la fabricación de materiales de construcción con estas características.

4.- Residuos y subproductos industriales

El 50% de los residuos generados provienen de la industria y construcción.
Es necesario analizar los focos de producción y acumulación de residuos y estudiar sus propiedades para transformar los subproductos industriales en materias primas potenciales en la fabricación de materiales.

Analizando la situación actual en España, sabiendo que casi el 50% de los residuos generados provienen de la industria y la construcción, se observa que desde los años 60 y 70, en los cuales se inició la industrialización, se generaron unos "puntos calientes" de contaminación que a fecha de hoy siguen siendo grandes focos de acumulación de residuos.

En 2009, 12 de las 191 instalaciones industriales que generaban más contaminación atmosférica estaban en España [61]. Entre los focos de contaminación importantes están la Bahía de Algeciras al sur de la Península Ibérica y los polos químicos de Huelva en Andalucía y Tarragona en Cataluña. La contaminación es especialmente alta en Huelva, que se considera una de las zonas más contaminadas de la Unión Europea. Se considera que la bahía de Algeciras, sede de muchas instalaciones industriales, concentra los niveles de contaminación por hidrocarburos más elevados de España [21].

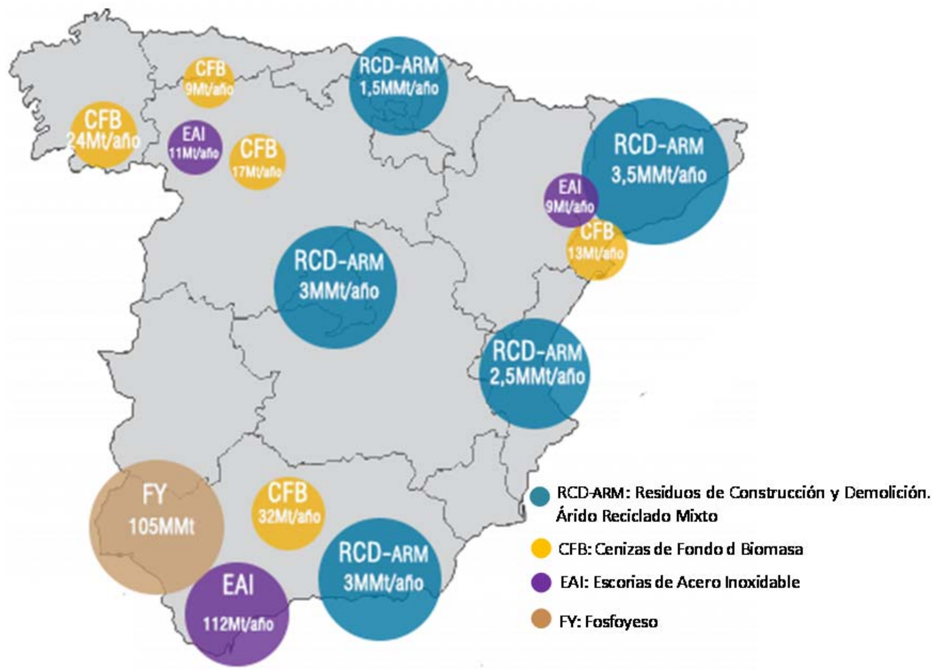

Figura 2.18: Generación anual de residuos estudiados en España

El gran volumen de residuos industriales y de construcción generados sumado a los efectos negativos sobre el medioambiente convierte la necesidad de gestionarlos adecuadamente en una prioridad. Actualmente se marca fundamentalmente el objetivo de “residuo cero”, lo que conlleva la búsqueda de que las actividades desarrolladas por el ser humano no generen ningún tipo de residuos, convirtiéndolos en subproductos reutilizables.

Actualmente, la gran mayoría de los países se encuentran muy lejos de este objetivo “residuo cero”. Según datos estimados por la OECD (Organisation for Economic Cooperational and Development) [62], los residuos generados mundialmente superan los 10000 millones de toneladas anuales. Únicamente en Europa se genera el 20% de la totalidad de estos residuos [63], produciéndose en España más de 60 millones de toneladas/año [64]. Estos números tan elevados muestran que el desarrollo de una correcta gestión de residuos es fundamental para la consecución de este objetivo.

Las políticas aplicadas se basan en los principios de acción preventiva, que consisten en reducir la producción de residuos, así como, la reducción de materiales peligrosos en ellos.

Para la aplicación de estos principios deben considerarse no únicamente factores que consideren soluciones menos perjudiciales para el medio ambiente, sino ha de tenerse en cuenta paralelamente soluciones favorables económicas y socialmente.

Los distintos organismos están desarrollando medidas que fomenten esta correcta gestión de residuos basándose en el incremento de la reutilización y reciclado mediante un aumento de costes de eliminación de residuos y explotación de recursos naturales. Así como, potenciar el uso de productos menos contaminantes que procedan de materiales valorizados entre los consumidores mediante la formación, consiguiendo modificar los modelos de consumo establecidos actualmente.

Las principales actividades que engloba la gestión de residuos son:

- Identificación y caracterización en el lugar de producción. Se debe identificar el grado de peligrosidad en relación a la manipulación, manejo, acondicionamiento y etiquetado para recuperación o eliminación.
- Almacenamiento en el lugar de origen antes de su recogida.
- Recogida. Mediante la que se realiza la clasificación, agrupación y preparación para transporte.
- Transporte a su destino final.
- Almacenamiento (no podrá superar un año si el fin es la eliminación, dos años si es valorización y debe ser almacenado un tiempo inferior a seis meses si es un residuo peligroso)
- Valorización, reciclado, recuperación
- Eliminación

Son necesarias nuevas estrategias de caracterización, control y seguimiento del ciclo global de residuos en la industria para mejorar las técnicas de tratamiento y control de calidad de los residuos. De esta forma, un avance en el conocimiento de las propiedades de cada uno de los residuos generados es esencial para optimizar su utilización.

Nos centramos en el conocimiento de los grandes focos de producción de residuos industriales en Andalucía.

4.1. Cenizas de Biomasa

Las políticas europeas y mundiales llevan centrándose años en el enfoque de la bioenergía como una alternativa a la energía fósil debido a los problemas de calentamiento global que se originan principalmente de la combustión de combustibles fósiles. Por lo tanto, recientemente se han llevado a cabo extensas investigaciones en todo el mundo para mejorar el uso de biomasa en lugar de los combustibles fósiles para la conversión de energía [65].

La Directiva [66] relativa al fomento del uso de la energía procedente de fuentes renovables, define la biomasa como *"la fracción biodegradable de los productos, desechos y residuos de origen biológico procedentes de actividades agrarias (incluidas las sustancias de origen vegetal y de origen animal), de la* silvicultura y de las industrias conexas, incluidas la pesca y la acuicultura, así como la fracción biodegradable de los residuos industriales y municipales". Entre la amplitud de residuos de diferentes fuentes de generación que contempla esta definición se observa que la tasa más elevado proviene de la biomasa agrícola, por lo que consideramos el estudio de las cenizas procedentes de la combustión de este tipo de biomasa.

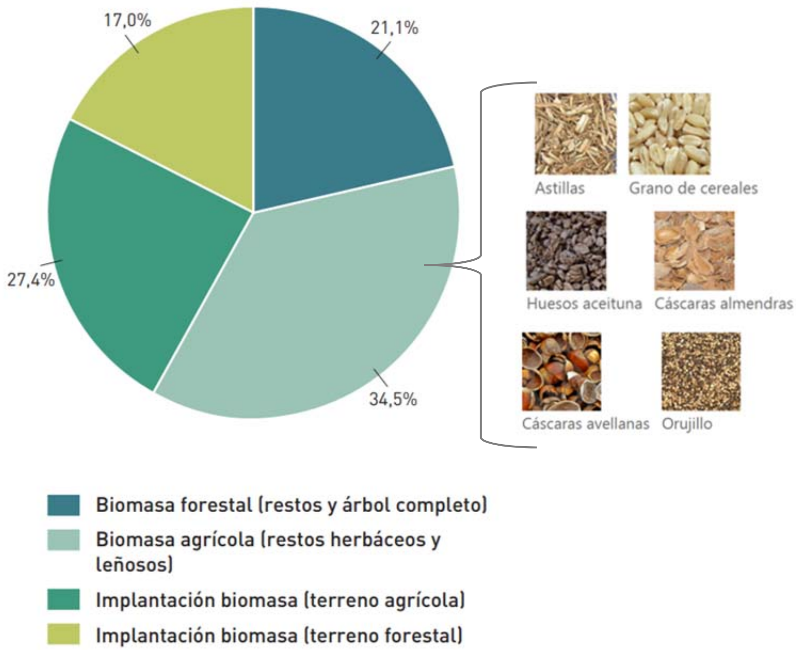

Figura 2.19: Distribución de biomasa potencial disponible. [67]

A pesar de que la utilización de biomasa se considera una energía limpia, como producto de esta combustión se generan grandes cantidades de ceniza. Aproximadamente 476 millones de toneladas de ceniza de biomasa (CB) se pueden generar en todo el mundo anualmente si se supone que la biomasa quemada es de 7 mil millones de toneladas con un rendimiento medio de ceniza del 6,8% en seco [68]. Esta cantidad es comparable a la de las cenizas de carbón, es decir, aproximadamente 780 millones de toneladas producidas por año en la actualidad [69]. La perspectiva actual de utilización de biomasa como combustible alternativo al fósil y los porcentajes impuestos para el incremento de su utilización llevará a la generación de grandes cantidades de CB. Por tanto, este residuo debe ser estudiado para evitar su acumulación y dar una alternativa de uso que lo convierta en un subproducto potencial. Basándonos en estudios previos, la presente Tesis Doctoral se basa en la reutilización de CB procedente de olivos (cultivo agrícola mayoritario en Andalucía) como material cementante y estabilizador de suelos.

4.1.1. Generación de energía y residuos producidos por la biomasa

Centrándonos en el concepto de sostenibilidad, se establecen unos objetivos mínimos para la utilización de fuentes de energía renovable para 2020. Concretamente, la Directiva tiene como objetivo que el 20% del consumo de energía en la Unión Europea proceda de fuentes renovables. España implanta estos objetivos.

Andalucía es la región española con mayor producción y consumo de energía renovable procedente de biomasa. Destaca la biomasa del olivar entre todas las demás, ya que la producción de aceite de oliva, uno de nuestros productos más preciados, es fuente además de numerosos subproductos con una importante aptitud energética.

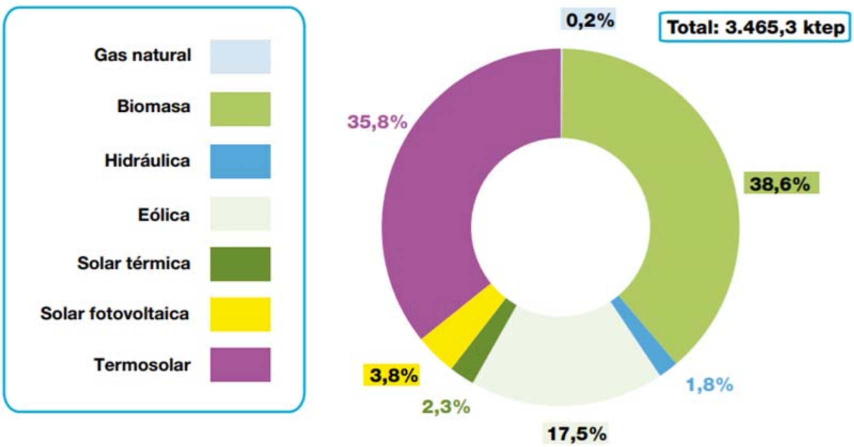

Figura 2.20: Estructura de producción de energía en Andalucía en 2016. [70]

Para el estudio de las cenizas generadas en la combustión de biomasa se debe considerar el proceso de producción de energía para entender las características del residuo resultante. Esencialmente, una planta de biomasa está compuesta por los siguientes elementos esenciales para la generación de energía: tolva de suministro, línea de combustible, parrilla de combustión, pistones hidráulicos y sistema de evacuación. La biomasa se introduce en el sistema mediante un proceso automático de alimentación desde el punto de almacenamiento. Tras la finalización del proceso, el residuo generado se elimina del sistema mediante un proceso de evacuación en forma húmeda generando un acopio húmedo [71].

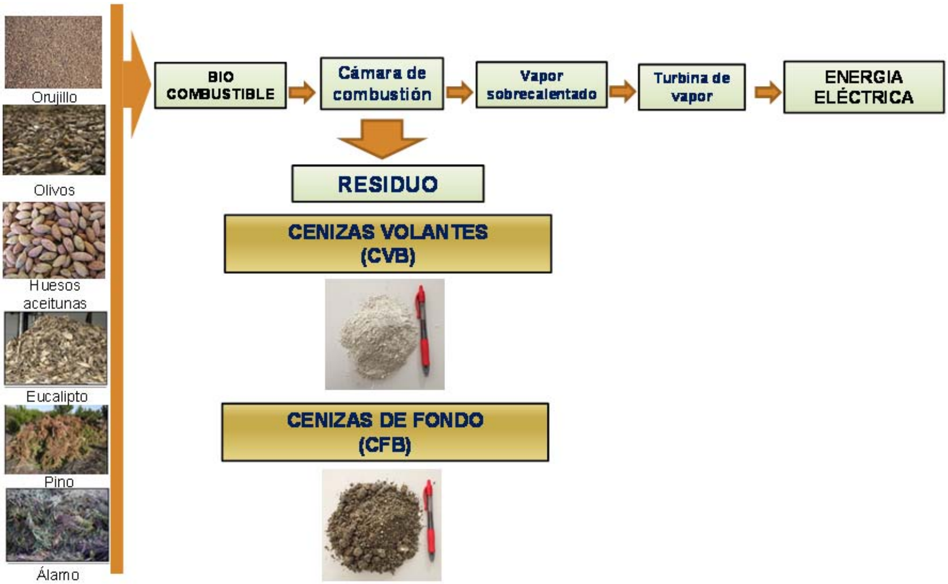

Figura 2.21: Proceso de producción de energía con biomasa y residuos generados

Los residuos generados en el proceso de combustión son dos:

Cenizas volantes (CVB): compuestas por partículas que son arrastradas por la corriente de gas hacia el exterior de la cámara de combustión [72]. Este tipo de cenizas se caracteriza por ser una material fino, aproximadamente el 70% de sus partículas son inferiores a 75 µm [73].

Cenizas de fondo (CFB): compuestas por partículas gruesas no quemadas producidas en la parrilla, en la cama inferior y en la cámara de combustión primaria. Este tipo de cenizas se mezcla con impurezas como arena, piedras y barro o con material de cama en las plantas de combustión de lecho fluidificado [23].

Aunque se emplean en cierta medida como fertilizantes, ambos residuos se valorizan en tasas muy bajas, por lo que mayoritariamente son depositados en vertederos. La presente Tesis Doctoral se centra en el estudio de las CFB debido a que es el residuo menos aplicado de los dos generados y es necesario estudios sobre su viabilidad de uso.

4.1.2 Aplicación ceniza de fondo de biomasa

Figura 2.22: Aplicaciones de CFB según Catálogo de Residuos utilizables en construcción. [35]

Desde el año 2014, las CFB están dentro del catálogo de residuos utilizables en construcción.

La utilización de las cenizas procedentes de la combustión de biomasa está condicionada por sus propiedades físico-mecánicas. Debido a que las CFB están formadas por partículas altamente porosas y de textura rugosa, presenta una baja densidad, siendo un material idóneo como sustituto en hormigones aligerados, además de ser características esenciales para su utilización en materiales con propiedades aislantes térmicas. Por otra parte, su alto contenido en SiO_2 y CaO, dotan a las CFB de unas características puzolánicas que llevan a estudiar su utilización como material de construcción con capacidad cementante. Las limitaciones en el uso de este residuo se derivan fundamentalmente de su exclusión en la normativa vigente y sus características físico-químicas. Debido a esas propiedades las CFB han sido estudiadas en las siguientes aplicaciones:

- **Bases y sub-bases de carreteras.** El estudio de las propiedades físicas y químicas desarrollado por [71] determinó la viabilidad de uso de las CFB como material de relleno en el núcleo de terraplenes de carretera ajustándose a las prescripciones técnicas del PG-3. En esta línea, se desarrollan los estudios de aplicación de CFB en materiales tratados con cemento para la conformación de base y sub-base de carretas [45]. Se observaron propiedades cementantes de las CFB que mejoran el comportamiento mecánico del material.

- **Hormigón.** Debido a sus propiedades químicas se han evaluado las CFB como sustituto de cemento y árido natural en la fabricación de hormigones, [74] observando que para ciertos porcentajes de sustitución no se comprometen las propiedades mecánicas de los hormigones. Beltrán et al. [49] investigaron dosificaciones óptimas para la aplicación de CFB como sustituto de cemento y arena en la fabricación de hormigones no estructurales. Se ha demostrado que tratamientos sencillos como la extracción de partículas ligeras de las CFB incrementan las propiedades mecánicas y de durabilidad de los hormigones fabricados [75].

- **Morteros.** Debido a las características físicas que presentan las CFB han sido estudiadas como árido y material cementante en la fabricación de morteros. Considerando estas propiedades físicas se llevó a cabo un estudio de la influencia del tamaño de partículas y su efecto en los morteros de cemento en diferentes dosificaciones [76].

Las propiedades de resistencia mecánica, durabilidad y trabajabilidad de morteros con CFB como sustitutos de cemento fueron estudiados por varios autores [77-80]. Demostrando que para ciertas dosificaciones y tratamientos de las CFB se obtienen resultados positivos para su utilización como árido o material cementante.

Basándonos en los resultados obtenidos en investigaciones, que siendo escasas, han mostrado que las CFB poseen propiedades físicas y químicas que demuestran su viabilidad de uso en diferentes materiales de construcción. Mediante esta investigación se ha profundizado en el estudio de sus propiedades cementantes y en la evaluación de la viabilidad de uso en diferentes materiales en base cemento.

4.2. Escorias de acero inoxidable

Otro de los objetivos planteados por la presente Tesis Doctoral es la evaluación de las escorias de acero inoxidable (EAI) procedentes de la fábrica Acerinox, ubicada en Los Barrios. El acero inoxidable es uno de los productos más sostenibles cuya producción se basa mayoritariamente en el reciclado de materiales. Las empresas del grupo Acerinox reciclan millones de toneladas de chatarra para producir acero, que al final de su vida útil serán de nuevo recicladas. Por este motivo, para cerrar el ciclo de reciclaje y compromiso con el medioambiente se plantea el presente proyecto, debido a la problemática que presenta la generación de escorias en la producción de acero inoxidable y su acumulación.

4.2.1. Fabricación de acero inoxidable y residuos producidos

El proceso de fabricación del acero en las acerías de arco eléctrico está dividido en dos etapas: metalurgia primaria o fusión, fase en la que las materias primas son fundidas, siendo estas materias primas fundamentalmente chatarra de hierro o acero y adicionalmente reducidas cantidades de fundición, mineral de hierro y de ferroaleaciones [81]. Y una segunda fase denominada metalurgia secundaria o afino.

El tipo de acero fabricado queda definido en función de las materias primas utilizadas y el contenido de carbono.

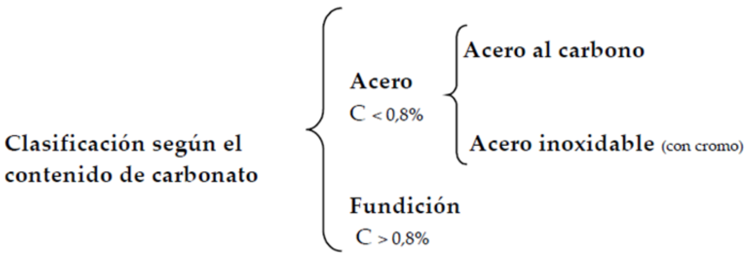

Figura 2.23: Tipos de aceros

En el proceso de fabricación del acero es necesario considerar la forma de producción. La Fábrica de Acero de Acero Inoxidable Acerinox S.A.U. dispone de los siguientes equipos:

- Tres hornos eléctricos, donde se funden las materias primas y se obtiene el acero líquido.
- Dos convertidores AOD, donde se realiza el afino, obteniéndose los niveles deseados de los diversos elementos de aleación.
- Colada continua de desbastes, cuya finalidad es convertir el acero líquido a sólido.
- Colada continua de palanquillas.

La capacidad de producción de Acería asciende a 1.067.400 Tm/año.

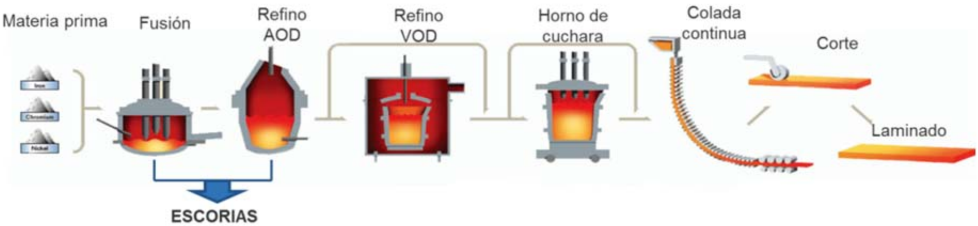

Figura 2.24: Fabricación del acero en horno eléctrico

Tras años de fuertes crecimientos, se han consolidado las producciones de acero. La producción mundial de acero inoxidable en 2015 fue de 41,7 millones de toneladas, una cifra muy similar a la de 2014.

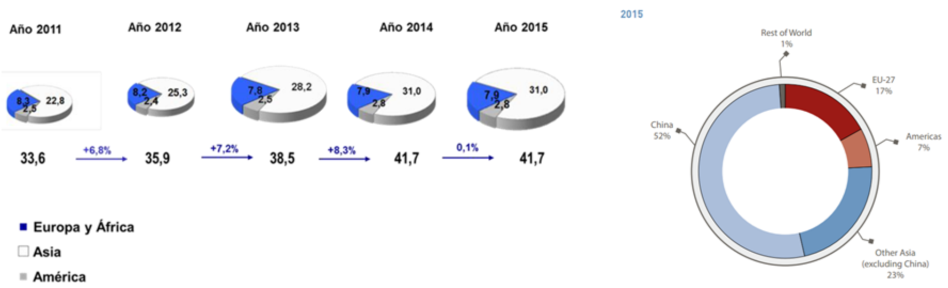

Figura 2.25: Evolución producción mundial (millones Tm). (Fuente: International Steel Slag Forum (ISSF))

Se deben tener en cuenta que en España funcionan actualmente 24 acerías de horno eléctrico de arco (14 de ellas en el País Vasco), que produjeron en el año 2014 un total de 13,6 Mt de acero de las cuales: acero común o especial: 12.420.000 t y acero inoxidable: 1.103.000 t [82]. La planta de producción de acero inoxidable más importante de España se encuentra en Andalucía, concretamente en la fábrica de Acerinox, situada en el T.M. de Algeciras. Esta planta produce alrededor del 80% del acero inoxidable de España, generando un porcentaje similar de residuos de escoria respecto al resto de España. Nuestro país es un alto productor de acero, situándose como la tercera productora de acero dentro de la Unión Europea.

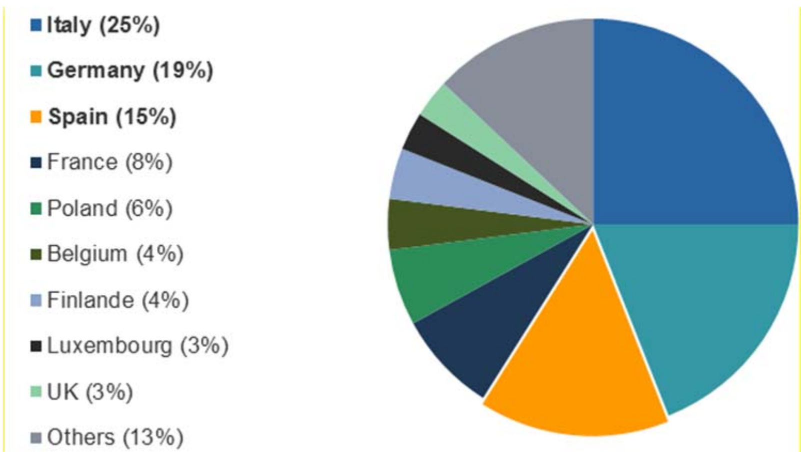

Figura 2.26: Producción acero en horno de arco eléctrico. (Fuente: World Steel Association)

Una da las problemáticas fundamentales de la fabricación de acero inoxidable es la generación de diferentes tipos de residuos durante su producción.

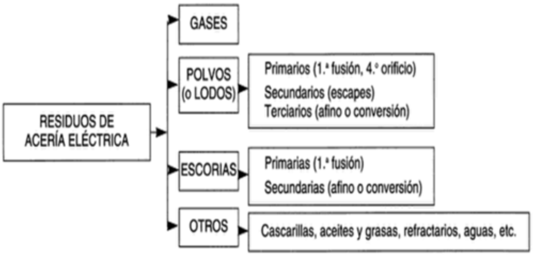

Figura 2.27: Tipos y volumen de residuos de acería eléctrica

Los denominados “residuos de Escorias de Acero Inoxidable” (EAI) son el subproducto objeto de esta Tesis Doctoral, ya que en la actualidad es conducido a vertedero el 76% de la producción sin ningún tipo de tratamiento que optimice el residuo y su aprovechamiento [83], debido a que presenta contenidos elevados en ciertos elementos perjudiciales como el Cromo, Manganeso o Magnesio. Este residuo es el que se genera en mayor volumen.

Todo ello pone de manifiesto la situación crítica de este residuo debido a las altas cantidades depositadas en vertedero, con el consiguiente impacto ambiental, además de la pérdida de oportunidad de dar salida a un residuo que ya está siendo revalorizado en otros países.

Por lo tanto, mientras no se defina una solución concreta, empresas como Acerinox deben incurrir en unos gastos periódicos para su manejo y disposición en vertedero (transporte, utilización de maquinaria, uso de vertederos para su almacenamiento, etc) sin olvidar el impacto ambiental, económico y social derivado de su desaprovechamiento. El mismo problema existe en la Unión Europea, donde hay alrededor de 10 fábricas de acero inoxidable con producciones elevadas, y de la misma manera, las EAI que generan son trasladadas a vertedero casi en su totalidad.

De ahí el desarrollo de la presente Tesis Doctoral. El aumento en la producción de acero inoxidable y las grandes cantidades de escorias que genera la elaboración del mismo nos lleva analizar las aplicaciones llevadas a cabo hasta la fecha de este tipo de residuos para el planteamiento de esta investigación

4.2.2. Aplicación escorias acero inoxidable

Figura 2.28: Aplicaciones de EAI según Catálogo de Residuos utilizables en construcción. [35]

Desde el año 2013, las EAI están dentro del catálogo de residuos utilizables en construcción. Aunque este catálogo se centra en las escorias de acero de arco eléctrico sin profundizar en la aplicación y valorización de las procedentes de la fabricación de acero inoxidable.

La aplicación de las escorias de acero ha sido estudiada en diferentes campos. Según las estadísticas publicadas por Euroslag, los datos del año 2010 mostraron que el uso de las escorias de acería ascendió a 22,3 millones de toneladas. Siendo la construcción de carreteras la que asumió el mayor porcentaje, un 48%. Un 6% fue utilizado en la producción de cemento y un 3% en otro tipo de construcciones civiles.

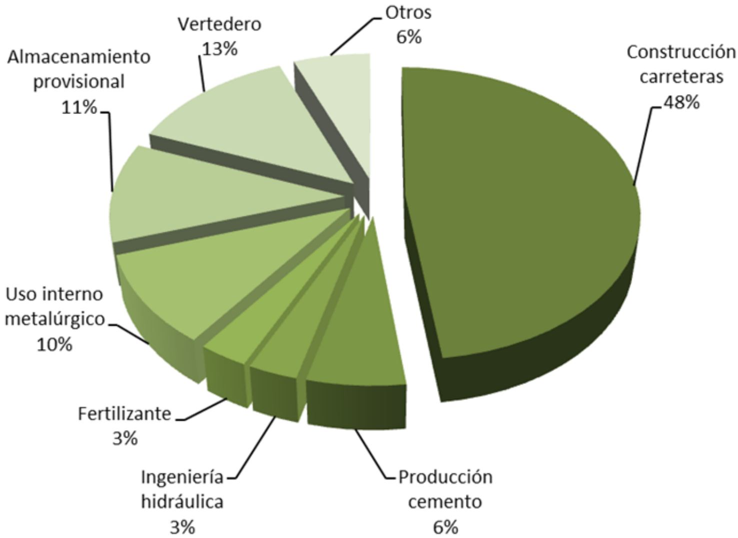

Figura 2.29: Aplicación escorias de acería.

Así, desde el punto de vista económico para los productores de acero, la consideración de la escoria como subproducto en lugar de residuo conlleva, además del ahorro del canon de vertido, poder comercializar directamente la escoria.

No se han realizado muchos estudios previos para la reutilización de las escorias de acero inoxidable. A continuación se detallan diversas aplicaciones llevadas a cabo para la aplicación escorias, tanto de acero, como de acero inoxidable.

- Bases, sub-bases y capa de rodadura de carreteras. Como se ha comentado anteriormente, el 48% de las escorias de acería utilizadas han sido aplicadas como material de construcción en sub-bases, bases o capas de rodadura de carreteras.

Debido a la alta resistencia a la fricción y a la abrasión, la escoria de acero está siendo más utilizada en carreteras, intersecciones y áreas de estacionamiento donde se requiere una alta resistencia al desgaste [84].

La utilización de la escoria blanca en este tipo de aplicaciones es inferior debido al contenido de finos. En el trabajo desarrollado por *[85]*, muestra que la combinación de ambas escorias en la construcción de pistas forestales es viable, mostrando una mejora de las propiedades que presenta el uso individualizado de cada una de ellas.

Otros estudios desarrollados por *[86]* demostraron la viabilidad de utilización de la escoria de acero como agregado en mezclas de asfalto.

Respecto al uso de escorias de acero inoxidable en este ámbito, las investigaciones realizadas son muy escasas. De Bock [87] describe la experiencia belga con el uso de escorias de acero inoxidable como agregado en el asfalto para la construcción de camino.

- Hormigón. Debido a la granulometría de las escorias, muchos estudios se han basado en la aplicación de este material como sustituto de la fracción fina en la fabricación de hormigones [88]; realizó un estudio sobre la aplicación de diversas escorias de acería en hormigón. Utilizando la fracción fina de escoria de acero inoxidable (AOD) en combinación con la escoria de Horno de Arco Eléctrico (EAF) como sustituto de arena en la fabricación de hormigón, observándose que no existían riesgos ambientales asociados a su uso.

Otros estudios llevados a cabo por [89]demostraron la posibilidad de sustitución del 100% de la fracción fina de áridos naturales por escoria de acero inoxidable con un tratamiento de oxidación, separación magnética y tamizado. Una sustitución del 100% produce mejores propiedades de hormigón endurecido, como la resistencia a la compresión, la resistencia superficial y la velocidad de ultrasonido.

Pellegrino and Gaddo, 2009 [90] demostraron que la escoria de EAF es adecuada para reemplazar los agregados naturales tradicionales en conglomerados, incluso en porcentajes altos y para tamaños medianos (hasta 2-4 mm de tamaño). Al igual que demostró [91]años antes en su estudio.

Respecto a la aplicación de EAI se han llevado a cabo estudios de utilización de estas escorias como sustituto parcial de árido grueso y de cemento en la fabricación de hormigones [92]. Obteniéndose resultados muy positivos que demuestran la resistencia de este material, resultando en hormigones con buenas características mecánicas. Las propiedades físicas y las resistencias mecánicas del hormigón hechas de agregados de escoria de acero inoxidable son ligeramente más altas que las del hormigón hecho de agregados silico-calcáreos [93].

- **Morteros.** Existen varios estudio [94] y [95] basados en la sustitución parcial o total del cemento y/o la arena por escorias de acería en los morteros.

El estudio realizado por Manos et al. [95] realiza una comparación de las propiedades físicas y durabilidad de morteros fabricados con escoria blanca como sustituto de arena y cemento frente a morteros convencionales. El porcentaje en peso de la escoria blanca en los morteros frescos está alrededor del 22%.

Por otro lado, los estudios realizados por [96] demostraron la posibilidad de sustitución en una tasa de reemplazo de hasta el 30% de cemento por escorias de acero inoxidable con diferentes tratamientos de finura obteniéndose mayores resistencias a compresión que los morteros fabricados con el 100% de cemento.

- **Adición en la fabricación de cemento.** Trabajos anteriores han estudiado las propiedades cementosas de la escoria de acero *[97]*. De acuerdo con estos estudios, este tipo de residuos podría ser utilizado en la fabricación de cemento. La industria del cemento está investigando posibles revisiones en el proceso de fabricación y en la selección de materias primas *[81]*. Actualmente, se producen 0,97 toneladas de CO_2 por cada tonelada de clinker *[98]*. El objetivo de la industria del cemento es reducir las emisiones de CO_2 en un 50% en 2050. Uno de los principales caminos para alcanzar este objetivo es reducir el contenido de clinker en cemento. El uso de residuos de escoria de acero inoxidable como material de cemento suplementario puede ser de gran interés en este contexto.

El valor potencial y la finura de las EAI sugieren que estos residuos se pueden utilizar como un material complementario en la fabricación de cemento *[99]*; *[100]*. Otros estudios *[101]* han discutido la aplicación de escoria de acero inoxidable en material de cemento, pero sólo con una tasa de reemplazo del 10% de cemento.

Uno de los países en los que se han llevado amplios estudios en la aplicación de estas escorias en la fabricación de cemento es Bélgica. Se han estudiado las propiedades de las EAI, aplicando procesos de activación de componentes para lograr un incremento de sus propiedades relativas a la hidraulicidad *[102]; [103]; [96]* desde varios puntos de vista.

En estudios previos se han aplicado diferentes métodos de activación, principalmente por tres vías: activación química, activación mecánica o activación térmica.

La escasez de estudios de aplicación de EAI en materiales en base cemento a pesar de las buenas características físicas y químicas que presentan llevan a desarrollar más en profundidad la viabilidad de uso de este material. Basándonos en las grandes cantidades generadas y la necesidad de valorización de este subproducto.

4.3. Fosfoyeso

Como se indicó en la presentación, el estudio de subproductos generados o acumulados en grandes cantidades nos lleva a la evaluación del fosfoyeso (FY).

En las proximidades de la ciudad de Huelva en Andalucía desde hace aproximadamente 50 años existe un gran complejo industrial químico, en el que entre sus actividades se encontraba la producción de ácido fosfórico para la fabricación de fertilizantes, detergentes, etc. El proceso de fabricación de este producto se basaba esencialmente en el ataque de la roca fosfática con ácido sulfúrico, esta reacción origina el ácido fosfórico y un subproducto denominado fosfoyeso.

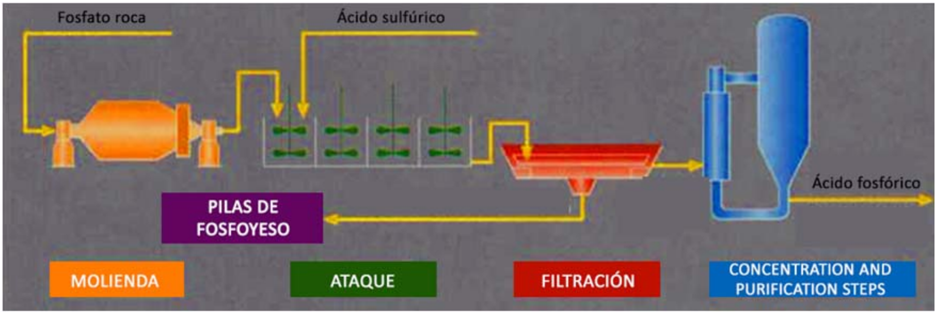

Figura 2.30: Proceso de producción de ácido fosfórico

El 80% del FY generado en la producción de ácido fosfórico desde sus comienzos hasta 1997 se apilaba en grandes balsas hasta una altura de 5 metros situadas en las marismas próximas a la desembocadura del río Tinto, el restante 20% era directamente vertido en la desembocadura del río Odiel. El cambio de política ambiental de 1998 llevó a la prohibición del vertido, desde esta fecha el 100% de este subproducto era apilado. Con esta nueva política, se disminuyó en cierta medida el impacto en el ecosistema acuático [104] así como, se procedió a la restauración de grandes zonas. La restauración ha consistido en el cubrimiento con una capa de suelo para minimizar el impacto visual y radiológico.

Actualmente, la zona de apilamiento cubre una extensión de 1200 hectáreas y en ella hay acumuladas 80 millones de toneladas. Pero esto no es un problema a nivel local, se estima que aproximadamente 3.000 Millones de toneladas de FY se encuentran almacenadas en más de 50 países en todo el mundo [105].

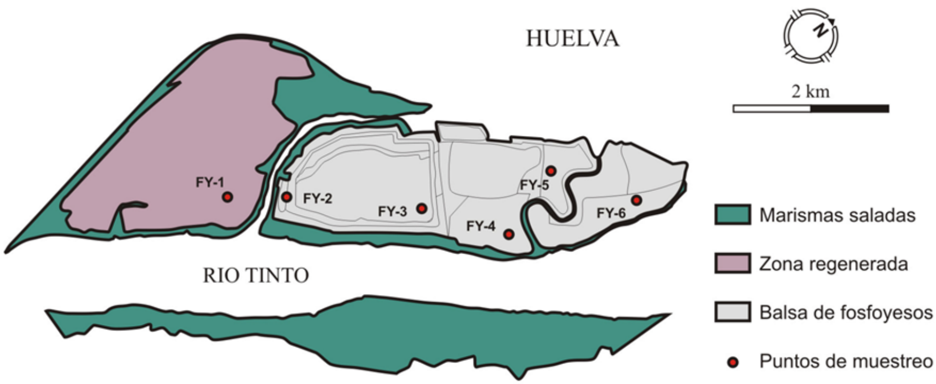

Figura 2.31: Plano con la disposición de las balsas de fosfoyeso en Huelva. [106]

Las presiones medioambientales, así como un aumento de los costos asociados al almacenamiento del FY están provocando que investigadores lleven a cabo trabajos de búsqueda para una mejor utilización de este material no solo a nivel local, sino a nivel mundial.

En 2014, Fertiberia, la empresa de fertilizantes encargada de la producción de ácido fosfórico en Huelva, presentó ante la Audiencia Nacional el "Proyecto Constructivo para la clausura de las Balsas de fosfoyesos". Un proyecto no ejecutado hasta la fecha en el que la empresa establece la necesidad de treinta años para la recuperación de las balsas. La recuperación propuesta consiste en la eliminación del agua presente en las balsas y la cubrición de las mismas mediante una capa de polietileno así como la revegetación de la zona.

Considerando escasa las líneas propuestas para la restauración de las balsas y analizando el creciente interés y preocupación por restauración ambiental que alienta la búsqueda de posibles aplicaciones de bajo costo de subproductos, la presente Tesis Doctoral abre una nueva línea de investigación evaluando la viabilidad de uso de estos subproductos como materia prima en la fabricación de materiales en base cemento.

4.3.1. Aplicación fosfoyeso

Figura 2.32: Aplicaciones de PG según Catálogo de Residuos utilizables en construcción. [35]

Desde el año 2014, el FY están dentro del catálogo de residuos utilizables en construcción.

Las propiedades del FY dependen de la naturaleza del mineral de fosfato, el tipo de proceso empleado, la eficiencia de la operación de la planta, el método de eliminación y ubicación y profundidad del vertedero o pila donde se descarga [107]. El FY es un material en polvo que tiene poca o ninguna plasticidad y está compuesto principalmente por de dihidrato de sulfato de calcio (> 90% de yeso) y fluorosilicato de sodio (Na_2SiF_6) [108]. Además, este subproducto se caracteriza por presentar altos contenidos de S y Ca.

Durante la última década, se han llevado a cabo varios estudios para verificar la viabilidad técnica de FY en materiales tratados con cemento o estabilización de suelos. Una cantidad muy pequeña de este subproducto se utiliza actualmente en las industrias de cemento y yeso.

Solo el 15% de la producción mundial de PG se recicla como material de construcción, agrícola fertilizantes o enmiendas de estabilización del suelo y como controlador establecido en la fabricación de Cemento Portland. El 85% restante se elimina sin ningún tratamiento.

Debido a sus propiedades químicas, se han desarrollados diferentes estudios basándose en su aplicación como enmienda de suelo en actividades agrícolas [109]. Además de como fertilizante, debido a su similitud con el yeso natural, se ha investigado la aplicación de este subproducto en diferentes ámbitos de la ingeniería civil.

Existen diferentes estudios sobre la aplicación de FY, la mayor parte de las investigaciones se centran en evaluar las propiedades mecánicas de materiales de construcción fabricados con FY, los métodos para la purificación del subproducto, su uso como regulador de fraguado y la contracción por secado causada en los materiales de construcción fabricados con FY.

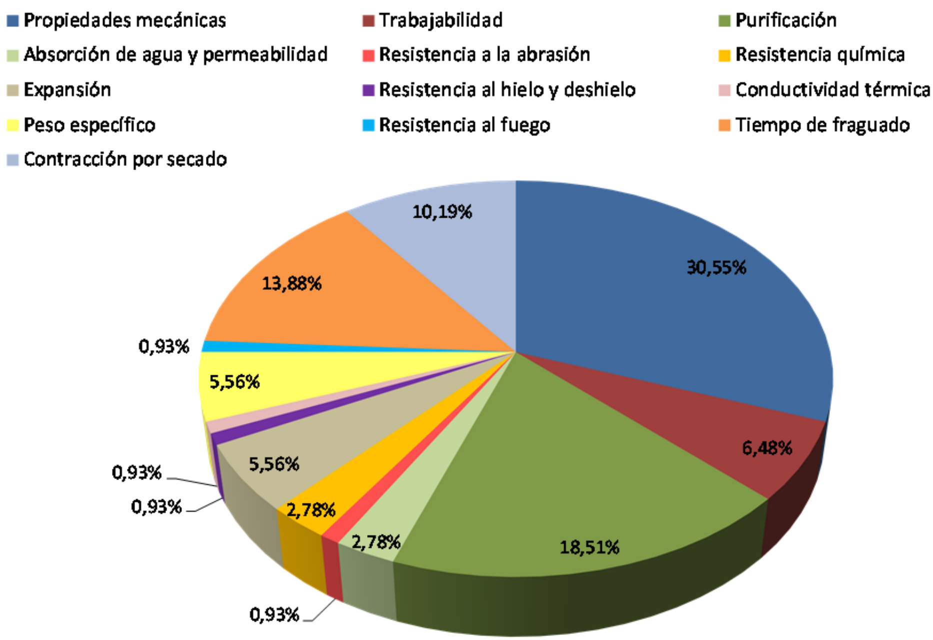

Figura 2.33: Efecto relativo del uso de FY en materiales de construcción en diferentes propiedades [110]

- Bases y sub-bases de carreteras. Estudios previos han demostrado que FY combinado con cemento se puede aplicar en la formación de capas de camino, reduciendo el porcentaje de cemento aplicado y manteniendo el comportamiento mecánico requerido en este tipo de materiales. Al aplicar FY hay dos importantes aspectos técnicos y ambientales que afectan de forma positiva; por un lado, su uso reduce el consumo de cemento con el consecuente beneficio ambiental, reduciendo las altas emisiones producidas en su fabricación; por otro lado, la aplicación de FY reduce el volumen de este subproducto almacenado en todo el mundo y, en consecuencia, su posible impacto en el medio ambiente y la salud de las personas.

Los primeros intentos de utilizar el FY en caminos se realizó en EE.UU. en la década de 1980. Los ensayos fueron realizados en Florida, en la construcción de carreteras para tráfico ligero y se demostró que este material, cuando se mezcla con el suelo no cohesivo, forma una base estable para pavimento bituminoso. Resultados similares fueron obtenidos al mezclar FY con cenizas de escorias de acero, actuando como material aglutinante en bases de carreteras. La resistencia a la rotura y el módulo de resiliencia de la ceniza de acero y el FY son equivalentes o superiores a los de esos materiales típicos de la base de la carretera, la estabilidad del agua de este material solidificado es mucho mejor que los materiales típicos utilizados [111].

La utilización de FY para la construcción de carreteras secundarias fue estudiada por diversos autores [112]. Se concluyó que el FY cuando se somete a compactación podría transformarse en un sólido de gran resistencia. Se podría usar de manera muy efectiva como aglutinante para estabilizar el suelo, reemplazar arcilla y árido en carreteras secundarias. Se construyó un tramo de base al esparcir 5 pulgadas de FY suelto en el suelo existente sobre el cual se colocó el hormigón. Este pavimento fue probado en cuanto a abrasión, durabilidad, contracción, deflexión in situ y monitoreo de la radiación.

El proyecto demostró que era adecuado el uso de FY para la construcción de aparcamientos, consiguiéndose adecuada resistencia para la mezcla y buen acabado superficial debido a la molienda del FY.

Además, han sido investigados su uso en rellenos de terraplenes [111, 113] limitando sus características físicas y fijando una compactación del núcleo de

FY, para evitar filtraciones de sulfatos u otros minerales al terreno, además de considerarse que debe tener un pH superior a 5. De la misma forma, se ha investigado su uso como material de relleno en minería [114], mostrando la viabilidad de uso de FY en combinación con residuos de construcción y demolición como relleno de pasta en base cemento.

Otros estudios más recientes se han basado en la aplicación de FY en mezclas asfálticas [115].

- Hormigón. La utilización de FY en hormigón no es una técnica nueva, Gutt lo propuso por primera vez, presentando un enfoque práctico para el uso de FY en hormigones [116].

Estudios actuales se han basado en la aplicación de FY en diferentes tipos de hormigón.

La aplicación de FY como árido en la construcción de losas de hormigón compactado con rodillo ha sido investigada [117]. Varias dosificaciones de FY fueron fabricadas y compactadas mediante vibrador. Este trabajo diseñó los espesores más adecuados para este tipo de pavimento. Se obtuvieron adecuadas propiedades mecánicas, así como, un retardo en el fraguado de las losas que compensó la contracción por secado del hormigón.

Otros estudios muestran la viabilidad de uso de FY en la fabricación de hormigón seco compactado, en los cuales se expone que mediante una dosificación adecuada se consiguieron excelentes resistencias a compresión [118]. La resistencia a compresión, flexión y flexotracción de hormigón con un 8% de reemplazo de cemento por FY no mostró variación respecto a un hormigón de control [119]. En otras investigaciones se demostró que las mezclas realizadas con un 10% de FY como sustituto del cemento incrementó los resultados de resistencia mecánica del hormigón [120, 121], considerando un factor clave la relación agua-cemento en cada una de las mezclas. Por tanto, se observa que hasta porcentajes del 8%-10% es posible el reemplazo de cemento por FY en la fabricación de hormigón, consiguiéndose un incremento de los resultados de resistencia mecánica.

- Morteros. Al igual que para la producción de hormigón, existen algunos estudios basados en la aplicación de FY en morteros de cemento. Se ha llevado a cabo estudios que sustituyen parte de la arena natural en la fabricación de morteros autonivelantes [122]; estos morteros se fabricaron con un 20% de cemento, 40% de FY y 40% de arena natural. La arena natural fue parcialmente reemplazada por 5%, 10% y 15% de FY. Los resultados representaron una disminución en la trabajabilidad inicial con la inclusión de FY disminuyendo a medida que se incrementó el porcentaje de FY debido a la mayor área específica de FY en comparación con la arena natural.

Se han llevado a cabo investigaciones con diferentes tratamientos de FY para mejorar las propiedades de los morteros de cemento; mediante el secado de FY a 60°C y 120°C se prepararon mezclas de mortero con Clinker, arena y reemplazos del 2%, 3% y 4% de Clinker por FY [123], los resultaron mostraron que mediante el uso de FY secado a 120°C los morteros de cemento presentaron valores de compresión y flexión similares a los de control.

La calcinación de FY mostró la viabilidad de uso de este subproducto como sustituto de Clinker hasta porcentajes de 8%, llevando a un aumento de la resistencia a compresión en los morteros de cemento fabricados con FY bajo determinadas condiciones de curado [124, 125]. Se observó que morteros curados al aire presentaron menores pérdidas en resistencia a compresión y flexión respecto a morteros que fueron curado en cámara húmeda [126].

- Adición en la fabricación de cemento. El uso del FY en la producción de cemento se debe a su similitud química con el yeso natural, materia prima utilizada en la producción de cemento como regulador de fraguado [127-129] o para reducir la temperatura de clinkerización en la fabricación de cemento Portland [108].

La presencia de impurezas ha dado lugar a muchas restricciones sobre las posibles aplicaciones de FY. Los estudios han demostrado que los fosfatos y fluoruros retrasan el tiempo de fraguado y reducen el desarrollo de la resistencia inicial del cemento. Además, se ha descubierto que la presencia alta de ALF^{5-} afecta negativamente a varios aspectos de la formación de cristales de yeso [130]. Por lo tanto, numerosos investigadores han recomendado procesos basados en lavado, secado y extracción química y térmica para hacer uso de FY en el proceso de fabricación de cemento.

El tratamiento térmico de FY ha resultado en la mejora de resistencias a flexión y compresión. Además, se encontró que el método de curado afecta en gran medida las fuerzas. Las muestras, que se curaron en una habitación húmeda, mostraron una resistencia menor en comparación con las curadas en el aire [126].

La revisión bibliográfica muestra los avances sobre la aplicación de FY en materiales en base cemento.

En España y concretamente en Huelva, este subproducto plantea una problemática por su acumulación sin ningún tipo de reutilización. Mediante esta Tesis Doctoral se ha ampliado el conocimiento de las propiedades que adquieren los materiales en base cemento fabricados con FY, abriendo una nueva línea de aplicación que demuestra la posibilidad de reutilización de este subproducto.

5.- Materiales base cemento eco-eficientes

El análisis realizado en el Estado del Arte pone de manifiesto que en consecuencia a las nuevas políticas de sostenibilidad y reutilización, los materiales de construcción, fabricados esencialmente con cemento, tienen que hacer frente a las necesidades técnicas a la vez que ser un material sostenible.

La sostenibilidad en la industria de la construcción se puede lograr a través de tres rutas diferentes (Figura 2.34), con reducciones en consumo de energía, reducción de emisiones y reducción de uso de recursos naturales.

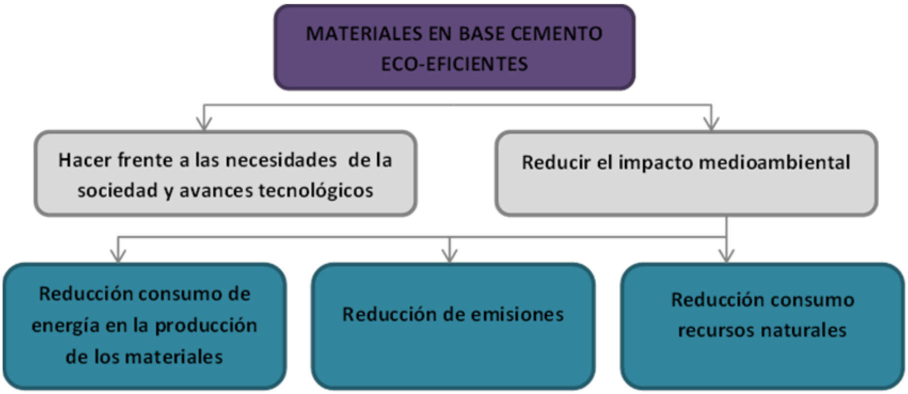

Figura 2.34: Estrategias principales para fabricación materiales base cemento eco-eficientes [131]

Las sociedades desarrolladas actuales requieren un entorno construido que es inimaginable sin el uso generalizado de materiales en base cemento.

En los últimos 65 años, la cantidad de cemento producido aumentó casi 34 veces [132], mientras tanto, el aumento de la población no ha llegado ni a triplicarse [133]. Se espera que la demanda de materiales a base de cemento continúe creciendo, y bajo la tecnología actual requerirá un aumento continuo de la producción de cemento.

Pero esta evolución y avance en los materiales y técnicas de construcción debe venir acompañado de un avance en sistemas de producción y materiales finales más sostenibles.

Analizando estos factores, la presente Tesis Doctoral ha abordado el estudio de una estrategia muy efectiva para reducir el impacto ambiental causado por la producción de materiales en base cemento basándose en la reducción del consumo de recursos naturales.

El aumento en el uso de los denominados materiales cementicios suplementarios, especialmente los subproductos, como escoria de alto horno y puzolanas de cenizas volantes, han recibido mucha atención de la comunidad de investigación [134] como una herramienta para mitigar los impactos ambientales [135], mejorar la durabilidad, e incluso para reducir costos.

Los resultados obtenidos muestran la posibilidad de fabricación de materiales en base cemento de forma sostenible. Mediante la valorización de materiales incorporados en la fabricación de morteros y hormigones como áridos convencionales o ligeros, una línea previamente estudiada [33, 136, 137]. Así como, el estudio de la incorporación de adiciones minerales o subproductos con actividad puzolánica [138, 139].

Cuanto mayor sea nuestra capacidad de innovación para producir materiales ventajosos desde el punto de vista técnico y ambiental, más viable será la mejora de las tasas de valorización en este campo. Es importante hacer un análisis integrado de problemas relacionados con la composición de los subproductos y las estrategias de valorización.

La necesidad de reciclar o reutilizar los residuos industriales junto con las buenas propiedades que se han encontrado en algunos materiales de construcción fabricados con estos subproductos, motivan la búsqueda de nuevas formas viables para aplicar algunos residuos industriales como materia prima alternativa en la producción de materiales en base cemento.

Por ese motivo, la presente Tesis Doctoral evalúa la aplicación de nuevos materiales cementicios suplementarios procedentes de diferentes subproductos industriales.

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CAPÍTULO III

OBJETIVOS

OBJETIVOS

El objetivo principal planteado en la presente Tesis es el estudio de la viabilidad de uso de subproductos industriales, tales como, áridos reciclados procedentes de residuos de construcción y demolición y cenizas de fondo procedentes de la combustión de biomasa, escorias de acero inoxidable y fosfoyeso para su aplicación en materiales en base cemento.

Para la consecución del objetivo principal planteado, se establecen las líneas de investigación expuestas en el Capítulo I. Estas líneas de investigación se plantean con el fin de cumplir los siguientes objetivos específicos:

1. **Estudio de las propiedades físicas y químicas** de los subproductos industriales (ARM, CFB, EAI, FY). Evaluando características básicas del material (granulometría, composición, coeficiente de los Ángeles, absorción, densidad, contenido en sulfatos solubles en agua y en ácido, mineralogía, etc.), analizando la influencia que conlleva su aplicación en las propiedades físicas, el comportamiento mecánico y durabilidad de los materiales en base cemento.

2. **Evaluación de diferentes tratamientos para mejorar las propiedades** de los subproductos industriales como materia prima en la fabricación de materiales en base cemento. Para ello, se lleva a cabo el procesamiento de CFB, EAI y FY mediante métodos de trituración, calcinación, lavado, extracción de partículas ligeras, etc. Desarrollando el estudio en la variación de sus propiedades físico-químicas y la influencia del tratamiento en las propiedades físicas, el comportamiento mecánico y durabilidad de los materiales en base cemento fabricados.

3. **Análisis de la capacidad cementante de los subproductos industriales mediante el estudio de las propiedades físico-químicas, comportamiento mecánico, durabilidad y tasa de reemplazo** en materiales en base cemento fabricados.

    3.1. Hormigones ligeros. Evaluación mediante ensayos de densidad y absorción de las propiedades físicas adquiridas por estos hormigones aligerados fabricados con ARM y CFB frente a hormigones convencionales. Análisis del comportamiento mecánico y de durabilidad de hormigones de acuerdo a la aplicación diferentes tasas de incorporación de ARM y CFB para posibilitar el uso de los subproductos en hormigones con características especiales y evaluar la tasa de reemplazo óptima.

3.2. Estabilizador de suelo. Estudio de la aplicación de CFB en sub-bases de caminos y en caminos rurales como estabilizador de suelo mediante la evaluación de las propiedades mecánicas y mineralógicas de diferentes mezclas.

3.3. Morteros de cemento. Análisis de las propiedades físico-químicas, mecánicas y de durabilidad adquiridas por morteros de cemento fabricados con diferentes subproductos industriales (CFB, EAI, FY). Se evalúa la influencia del tratamiento de los subproductos en el comportamiento de los morteros de cemento y la tasa de reemplazo óptima. Este estudio es ampliado con un análisis estadístico que se basa en el Análisis de Componentes Principales desarrollado para la evaluación de la aplicación de EAI estudiando el grado de asociación o discriminación entre tratamientos y porcentajes aplicados. Posteriormente, para estudiar la aplicación de FY se desarrolló este mismo estudio junto con un Modelo de Regresión Lineal para evaluar la influencia del porcentaje de adición y el tratamiento en las propiedades mecánicas de los morteros.

4. **Estudio de las posibles consecuencias medioambientales** que puede conllevar la utilización de subproductos industriales en ingeniería civil. Se lleva a cabo ensayos de lixiviación al material en estado granular y ensayos de evaluación de lixiviación de metales pesados en materiales monolíticos para evaluar el comportamiento medioambiental del subproducto dentro de una matriz cementante.

CAPÍTULO IV

METODOLOGÍA

IV METODOLOGÍA

Para conseguir los objetivos expuestos se desarrolla la metodología expuesta a continuación en 3 fases diferenciadas. Estas fases son descritas en orden cronológico seguido durante la realización de la Tesis Doctoral.

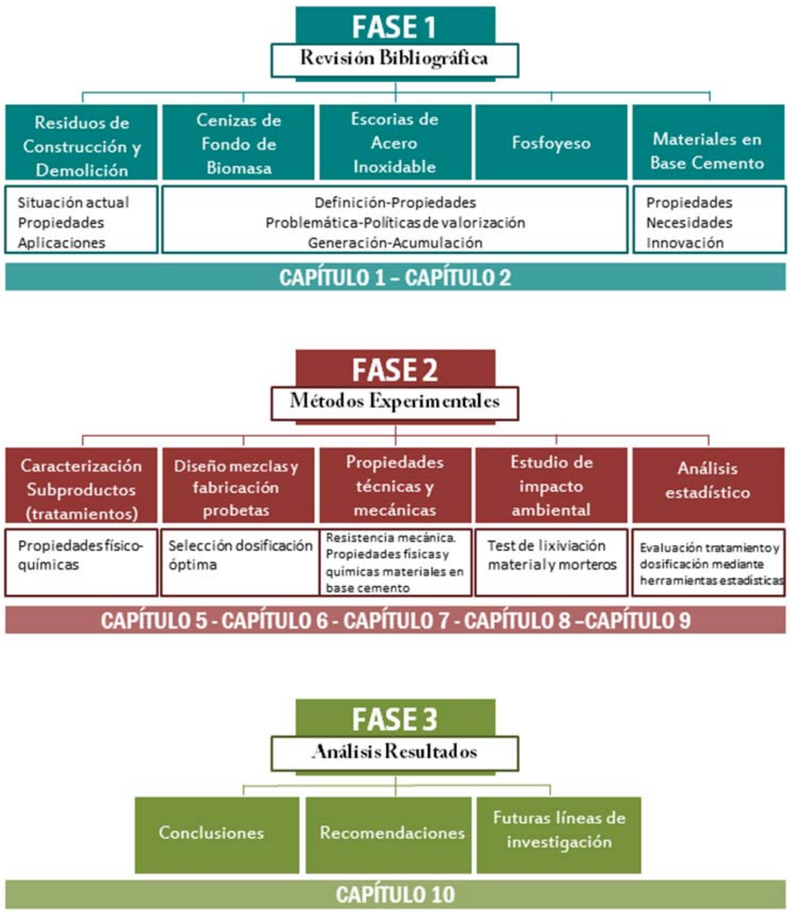

Figura 4.1: Metodología seguida en la presente Tesis Doctoral

Fase 1: esta fase se centra en el estudio preliminar de la situación actual mediante una exhaustiva revisión bibliográfica. El análisis de los antecedentes y la evaluación de estudios previos mostrada en el Capítulo I y Capítulo II ha llevado a plantear la metodología de trabajo y objetivos a conseguir mediante la presente Tesis Doctoral.

Fase 2: corresponde al desarrollo de la fase experimental (Figura 4.2).
Esta fase se divide en 6 bloques diferenciados.

- **Bloque 1:** Caracterización física y química de los subproductos industriales, para determinar la viabilidad de uso en materiales en base cemento de acuerdo con las propiedades obtenidas. Mediante el desarrollo de esta primera sub fase se pretenden conseguir el Objetivo 1. Los resultados obtenidos se muestran en las diferentes publicaciones en función al tipo de subproducto estudiado.

  CFB: **"***Feasible use of biomass bottom ash as addition in the manufacture of lightweight recycled concrete."*

  "Feasibility of using olive biomass bottom ash in the sub-bases of roads and rural paths."

  EAI: **"***Effects of stainless steels slag waste as a replacement for cement in mortars. Mechanical and statistical study."*

  FY: *"Phosphogypsum treated to be used as alternative set regulator and mineral addition in cement production."*

- **Bloque 2:** Se llevan a cabo procesos sencillos de calcinación, trituración, lavado, eliminación de partículas ligeras y diferentes combinaciones entre ellos para la evaluación de la influencia de este tipo de tratamiento en las propiedades físico-químicas de los subproductos industriales y como contribuye su uso en la mejora de las propiedades cementantes de morteros de cemento. Se pretende alcanzar el Objetivo 2 y los resultados obtenidos se muestran en las diferentes publicaciones en función al subproducto estudiado.

  CFB: *"Effects of treatments on biomass bottom ash applied to the* *manufacture of cement mortars."*

EAI: **"***Effects of stainless steels slag waste as a replacement for cement in mortars. Mechanical and statistical study."*

FY: **"***Phosphogypsum treated to be used as alternative set regulator and mineral addition in cement production."*

- **Bloque 3:** Fabricación de hormigón ligero mediante el uso de CFB y ARM como sustituto de áridos naturales. En función a los resultados obtenidos en el bloque 1, los cuales reflejan la baja densidad de las CFB, se lleva a cabo el estudio de la viabilidad de uso de estos subproductos industriales en diferentes tasas de reemplazo estudiando las características físicas que adquiere el hormigón ligero y su comportamiento mecánico y durabilidad. Mediante el desarrollo de este bloque se busca el cumplimiento del Objetivo 3.1. Los resultados obtenidos se muestran en la publicación **"***Feasible use of biomass bottom ash as addition in the manufacture of lightweight recycled concrete."*

- **Bloque 4:** Fabricación de mezclas de CFB con arcilla expansiva para evaluar la viabilidad de uso de este subproducto como estabilizador de suelo. Al igual que se desarrolla, en el bloque anterior, considerando las propiedades físico-químicas de las CFB analizadas previamente, y evaluando el comportamiento en la fabricación de hormigón. Se desarrolla el estudio de las propiedades físicas, mineralógicas y el comportamiento mecánico de diferentes mezclas de suelo expansivo con CFB para demostrar la posibilidad de aplicación de este subproducto como material estabilizador de suelo, comparándolo con estabilizadores utilizados tradicionalmente. Este bloque se centra en conseguir los el Objetivo 3.2 y los resultados obtenidos se muestran en la publicación *"Feasibility of using olive biomass bottom ash in the sub-bases of roads and rural paths."*

- **Bloque 5:** Estudio de las propiedades cementantes de diferentes subproductos industriales como sustituto de materias primas en la fabricación de morteros de cemento. El análisis de las características físico-químicas de los materiales aplicándoles o no tratamiento mostrados en el bloque 1 y 2 revelaron que estos subproductos poseían propiedades internas intrínsecas que posibilitaban su uso como un sustituto de cemento, del árido natural, incluso del yeso natural en la fabricación de cementos.

Por ese motivo se desarrollaron tres estudios diferentes evaluando cada uno de los subproductos industriales con los diferentes tratamientos. Se fabricaron morteros de cemento con diferentes dosificaciones para analizar la influencia de la aplicación de estos materiales en las propiedades físicas, comportamiento mecánico, durabilidad y mineralogía adquiridas. De esta manera, se obtuvo un porcentaje de sustitución y un tratamiento óptimo para cada uno de los subproductos, mostrando una mejora en las propiedades de los morteros fabricados.

Este bloque pretende alcanzar el Objetivo 3.3. Los resultados obtenidos se muestran en las diferentes publicaciones en función al subproducto estudiado.

CFB: *"Effects of treatments on biomass bottom ash applied to the manufacture of cement mortars."*

EAI: "*Effects of stainless steels slag waste as a replacement for cement in mortars. Mechanical and statistical study."*

FY: "*Phosphogypsum treated to be used as alternative set regulator and mineral addition in cement production."*

- **Bloque 6:** Estudio del impacto ambiental de CFB, EAI y FY. En este bloque se estudia el impacto medioambiental que causa la aplicación de los subproductos industriales mediante el análisis de lixiviados de metales pesados. Con este bloque se pretende conseguir el Objetivo 4. Los resultados obtenidos se muestran en cada una de las publicaciones en función al subproducto industrial analizado.

CFB: "*Feasible use of biomass bottom ash as addition in the manufacture of lightweight recycled concrete."*

EAI: "*Effects of stainless steels slag waste as a replacement for cement in mortars. Mechanical and statistical study.″*

FY: "*Phosphogypsum treated to be used as alternative set regulator and mineral addition in cement production."*

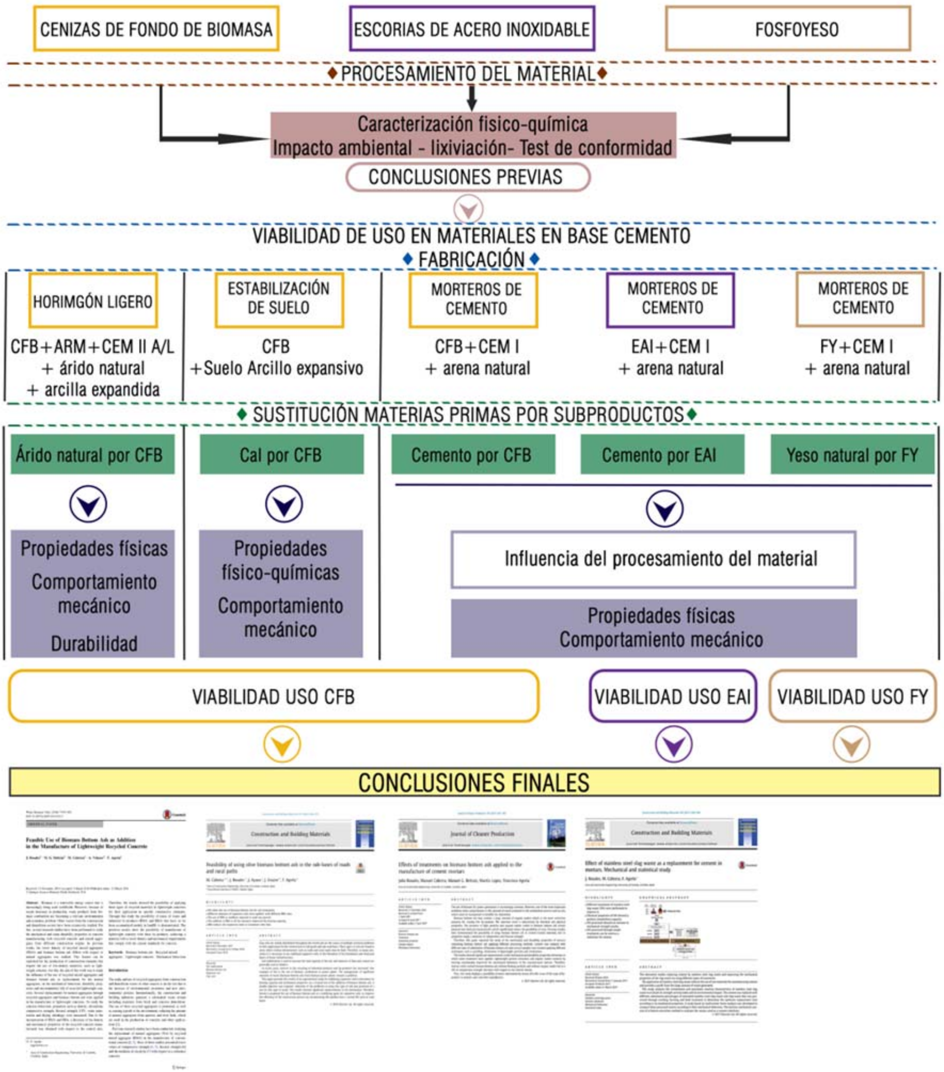

Figura 4.2: Desarrollo de la fase experimental

Fase 3: Basándonos en los resultados obtenidos en las fases anteriores se obtuvieron conclusiones y se establecieron una serie de pautas y recomendaciones para la aplicación de estos subproductos industriales en diferentes materiales en base cemento. Estas conclusiones y pautas fueron publicadas en revistas científicas, congresos internacionales, revistas técnicas, etc. Para el conocimiento de toda la comunidad científica, de forma que permita el avance en la aplicación de subproductos industriales en materiales en base cemento eco-eficientes y sirva de base para futuras líneas de investigación.

CAPÍTULO V

FEASIBLE USE OF BIOMASS BOTTOM ASH AS ADDITION IN THE MANUFACTURE OF LIGHTWEIGHT RECYCLED CONCRETE

Rosales, J., Beltrán, M. G., Cabrera, M., Velasco, A., & Agrela, F.

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V

FEASIBLE USE OF BIOMASS BOTTOM ASH AS ADDITION IN THE MANUFACTURE OF LIGHTWEIGHT RECYCLED CONCRETE

Rosales, J., Beltrán, M. G., Cabrera, M., Velasco, A., & Agrela, F. (2016). Feasible use of biomass bottom ash as addition in the manufacture of lightweight recycled concrete. Waste and Biomass Valorization, 7(4), 953-963.

Abstract

Biomass is a renewable energy source that is increasingly being used worldwide. However, because of recent increases in production, waste products from biomass combustion are becoming a relevant environmental and economic problem. Other wastes from the construction and demolition sectors have been extensively studied. For this, several research studies have been performed to study the mechanical and some durability properties in concrete manufacturing with recycled concrete and mixed aggregates from different construction origins.

In previous works, the lower density of recycled mixed aggregates (RMA) and biomass bottom ash (BBA) with respect to natural aggregates was studied. This feature can be exploited for the production of construction elements that require the use of low-density materials, such as lightweight concrete. For this, the aim of this work was to study the influence of the use of recycled mixed aggregates and biomass bottom ash, as replacements for the natural aggregates, on the mechanical behaviour, durability properties and environmental risk of recycled lightweight concrete. Several replacements for natural aggregates through recycled aggregates and biomass bottom ash were applied in the manufacture of lightweight concretes. To study the concrete behaviour, properties such as density, absorption, compressive strength, flexural strength, UPV, water penetration and drying shrinkage were measured. Due to the incorporation of RMA and BBA, a decrease of the density and mechanical properties of the recycled concrete manufactured was obtained with respect to the control mix.

Therefore, the results showed the possibility of applying these types of recycled materials in lightweight concretes for their application in specific constructive elements.

Through this study the possibility of reuse of waste and industrial by-products (RMA and BBA) that have so far been accumulated mainly in landfill is demonstrated. The positives results show the possibility of manufacture of lightweight concrete with these by-products, achieving a material with a lower density and mechanical requirements that comply with the current standards for concrete.

Keywords:

Biomass bottom ash, Recycled mixed aggregates, Lightweight concrete, Mechanical behavior

5.1.- Introduction

The study and use of recycled aggregates from construction and demolition wastes or other sources is on the rise due to the increase of environmental awareness and new environmental policies. Internationally, the construction and building industries generate a substantial waste stream including materials from brick and concrete demolition. The use of these recycled aggregates is promoted, as well as causing a profit to the environment, reducing the amount of natural aggregates from quarries and river beds, which are used in the production of concrete and other applications [1].

Previous research studies have been conducted, studying the replacement of natural aggregates (NA) by recycled mixed aggregate (RMA) in the manufacture of conventional concrete [2, 3]. Most of these studies presented lower values of compressive strength [4, 5], flexural strength [6] and the modulus of elasticity [7] with respect to a reference concrete.

With social and technological advances, the production of industrial waste is continuously increasing, and environmental considerations of reducing and recycling this waste have emerged. The construction industry is using recycled materials to produce green building materials for environmental protection.

The combustion of biomass has been introduced in recent years as a method of generating renewable energy. Therefore, the treatment and disposal of ashes produced by biofuel combustion have become an environmental and economic problem. The characteristics of ash from the combustion of biomass are highly variable and depend on the characteristics of the biomass (e.g., pruning olive, olive cake, and poplar) and the technology used for combustion [8–10].

There are many works that have studied the use of biomass fly ash (BFA) as addition in the manufacture of constructions materials [11]. However, fewer studies have incorporated the biomass bottom ash (BBA) in civil infrastructures; this industrial by-product is instead stored in landfills.

The positive results obtained by incorporation of BBA in the manufacture of concrete and recycled materials treated with cement [12, 13] and the lower density of this industrial by-product and the RMA leads to study of the possible application of these materials as substitutes for natural aggregates in the manufacture of lightweight concrete (LWC).

The demand for lightweight concrete in many applications of construction is increasing, owing to the advantage that lower density results in a significant benefit in terms of load-bearing elements [14]. On the other hand, the porosity of the material reduces the heat loss in buildings that decreases the consumption of energy. [15, 16].

The low density and high thermo-insulating capacity of LWC are its most distinct characteristics in comparison to normal weight-aggregate concrete [17]. Moreover, the reduction of the mass of the structure or building is of utmost importance to prevent seismic effects. In order to meet the requirements for buildings light weight concretes usually possess characteristics of high porosity, low density and relative high strength [18, 19].

The properties of LWC mainly depend on the amount and properties of the lightweight aggregates used; in this case; we have used expanded clay. Therefore, many studies have been conducted to examine how the aggregate properties affect the mechanical properties of lightweight aggregate concrete [20].

Generally, RMA has a lower density with respect to NA [21]. Enabling this feature get less dense concrete over conventional concrete. Previous studies of lightweight concrete by using different unit weight aggregates including lightweight crushed bricks, lightweight expanded clay, and normal-weight gravel without the use of natural fine aggregates (no-fines concrete), obtained positive mechanical properties [22].

There are several studies on using lightweight aggregate either in LWC production or lightweight concrete blocks [22–25]. Moreover, other previous studies have evaluated different waste for the production of lightweight concrete such as rubber particles [26], polystyrene foam (EPS) [27], crumb rubber from waste tires recycling [28] or incinerator bottom ash [29] with positive results in the physical and mechanical properties for a specific percentage of substitution. These earlier results lead us to propose this work.

Through this study has been evaluated the possibility of reusing BBA and RMA in several replacement rates to manufacture lightweight concrete. To know the nature of these materials, physical and chemical properties of BBA and RMA were determined. Additionally, physical (density, absorption and water absorption), mechanical (compressive, flexural strength and UPV) and water penetration under pressure and shrinkage of recycled lightweight concretes manufactured were studied. In addition, a study of the environmental effects of BBA were realised through the leaching test.

Through this study the manufacture of lightweight concrete with BBA and RMA was evaluated that will provide an advantage of reduction in dead weight of a construction, due to the decrease in density of these materials. In addition, economic and environmental advantages are expected through the use of LWC mixture manufactured with waste.

5.2.- Materials and Methods

Cement

Portland cement with limestone with high initial strength was used in this study (CEM II–A/L–42,5). All its chemical properties are summarised in Table 5.1.

Table 5.1: Properties of the cements

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Granul. 45 µm	Granul. 32 µm	Blaine E.S.	Loss of ignition
%	%	%	%	%	%	%	%	%	%	cm^2/g	%
18.22	4.27	3.06	62.21	0.9	3.17	0.70	0.26	11.4	21.6	4198	6.56

Biomass Bottom Ash

As a fine fraction replacement, BBA with nominal size of 10 mm was used (Figure 5.1). The power plants in the Andalusian Region burn approximately 40 % olive cake and 60 % wood biomass (poplar, olive and pine). BBA is a by-product generated from the combustion of biomass composed mainly of olive mash.

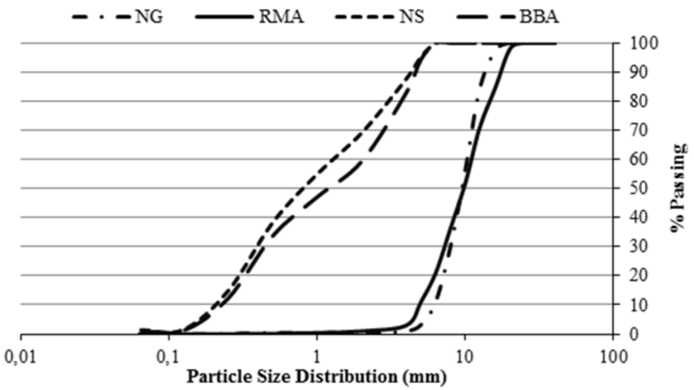

Figure 5.1: Particle size distribution curves

Physical and chemical characteristics of (BBA) depend on the types and quality of the biomass combusted and the performance of combustion [30, 31].

A low value of density was obtained due to the high porosity of the particles of BBA. In addition, high abrasion susceptibility was measured (Table 5.2). Also, absorption is an important factor to consider because many physical parameters of bottom ash are altered in the presence of excess water [32, 33].

Table 5.2: Physical and chemical properties of BBA

Properties	BBA
Density SSD (Kg/dm^3)	1.97
Water absorption (%)	26.6
Friability ratio (%)	29.6

Sulphur content (%)	0.23
Soluble sulphate (%SO3)	0.41
Chlorides (%)	0.19
Organic matter content (%)	4.12
Elemental content (%)	
Si	24.32
Ca	17.09
K	15.64
Mg	2.27
Fe	1.03
Al	0.98
Na	0.15
Ti	0.09

Incorporating BBA in lightweight concrete manufacturing may increase the pollutant potential of the product, presenting an environmental risk via ground water contamination. Previous works showed the polluting potential due to the leaching of heavy metals by this waste.

For this reason, before applying BBA in lightweight concrete manufacturing, a study was performed accordingto the European standard UNE-EN 12457-3-2002 to assess the leaching of heavy metals that produce this waste.

The extraction was obtained at a stage with an L/S of 10 l/kg. The contact time with deionized water was 24 ± 0.5 h. The solution was decanted, and the pH, conductivity and temperature were measured. In this study, the solution was filtered through a 0.45-m membrane filter, and subsamples of leachates from each material were collected. The samples were refrigerated until analysis.

To classify materials according to their possible negative environmental effects, the European Council Decision 2003/33/EC was adopted. This legislation imposes limits on the concentrations of various metals and anions resulting from leaching processes.

The concentrations of the following metals were determined in the leachates: arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), zinc (Zn), calcium (Ca), magnesium (Mg), Selenium (Se) and Antimony (Sb). The concentrations obtained were compared with the European limit values; a residue can be classified as an inert, non-hazardous or hazardous material.

Table 5.3 shows the classification of the material samples studied by comparing them with established legal standards for heavy metal concentration. The BBA were classified as non-hazardous according to the data obtained by the compliance test (Table 5.3).

Table 5.3: Concentrations of metals and sulphate on leachate at L/S = 10 l/kg and classification according to concentration on heavy metals

L/S=10	Metals (l/kg)												Classification
	Ni	Cu	Cr	Zn	As	Se	Mo	Cd	Sb	Ba	Hg	Pb	
BBA	0.03	0.18	0.36	0.03	0.18	0.05	0.28	0.00	0.03	0.02	0.05	0.00	Non-hazardous

According to the results, Figure 5.2 shows the limits of each heavy metal surpassed by BBA. Hg is identified as the most conflictive element. The concentration of Hg was presented as non-hazardous in analysis samples. Therefore, BBA was considered non-hazardous because the Hg leachate maximum concentrations exceeded the limits established by the Standard.

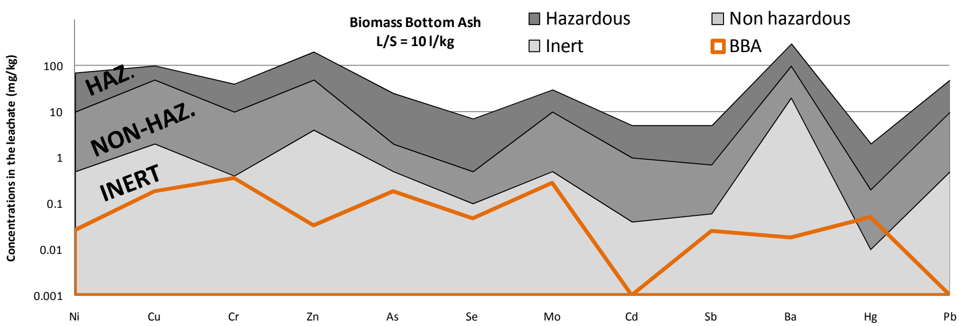

Figure 5.2: Concentration in leachate in BBA

Expanded Clay

Expanded clay (EC) is a brown lightweight aggregate produced by firing natural clay, which swells at 1000–1200 °C due to the action of the gases generated inside the mass [34, 35]. This material is typically used in the manufacture of LWC. The light weight of this product is largely attributed to a relatively high proportion of semiclosed pores, which can account for up to 90 % of the particle volume. The properties of this material are shown in Table 5.4. In this work, EC was applied in the different mixtures to compare the behaviour of LWC mixtures manufactured with several content variations of

RMA, BBA and EC.

Natural and Recycled Mixed Aggregates

Two types of natural aggregates (NA) were used in the manufacture of concrete: natural coarse gravel (NG) and natural sand (NS).

Recycled mixed aggregates (RMA) from the treatment of CDW in Gecorsa (Córdoba) were used in this research. This RMA is composed by different materials: asphalt, ceramic, concrete and mortar, natural aggregates, gypsum and impurities (wood, glass, plastic, and metal). The properties of the aggregates are summarised in Table 5.4, and their particle-size distribution is shown in Fig. 5.1.

According Figure 4.1, it can be deduced that all of the aggregates present continuous granulometry.

An important value to note is the density of saturated surface dry (SSD) obtained from each of the materials (Table 5.4). SSD density was higher in natural aggregates than in recycled aggregates and conversely, the absorption of RMA is greater is greater how it is verified in previous studies due to the presence of ceramic aggregates [21].

BBA has the lowest value of SSD<2 kg/dm3 (Table5.2). This type of waste has a lower density than recycled fine ceramic aggregate or furnace bottom ash [36]. For this reason, it is more appropriate to decrease the density of the concrete.

Table 5.4: Physical and chemical properties of recycled and natural aggregates

Properties	**NG**	**NS**	**EC**	**RMA**
Size (mm)	4-32	0-4	3-8	4-32
Density SSD (kg/dm3)	2.67	2.59	0.96	2.31
Absorption (%)	2.77	3.81	6.6	6.94
L.A. Abrasion Value (%)	24	-	-	33.4
Sulphur content (%)	<0.01	<0.01	<0.01	0.94
Soluble sulphate (%SO3)	<0.01	<0.01	<0.01	1.07
Chlorides (%)	0.09	<0.01	<0.01	0.06
Constituents of the aggregates (%)				
Natural aggregates	100	100	100	23.5
Crushed concrete particles	0	0	0	47.8
Ceramic particles	0	0	0	19.7
Asphalt particles	0	0	0	8.1
Others	0	0	0	0.9

Water-Reducing Admixture

A super-plasticiser additive (SP), type BASF Rheobuild 1222, was used. The objective was to reduce the mixing water and allowing the concrete to be manufactured with a low effective water/cement ratio (w/c) because of its high water reduction.

Concrete Mix Proportions

Eight batches were manufactured by applying various incorporation rates of RMA and BBA (Table 5.5).

Table 5.5: Lightweight concrete mix proportions (kg/m^3)

	DOSAGE (kg/m^3)									**Recycling factor**
	NG	NS	RMA	EC	BBA	Cement	Water	Additive	TOTAL	
Control										
100NA 0BBA	494.2	710.3	0	108.7	0	300	180	2.8	1793.2	**0.00**
Series 1										
50RMA 0BBA	247.1	710.3	217.8	108.7	0	300	180	3	1763.9	**20.4**
100RMA 0BBA	0	710.3	435.5	108,7	0	300	180	3	1734.5	**53.2**
0RMA 30BBA	494.2	497.2	0	108.7	163.3	300	180	3.3	1743.4	**14.8**
50RMA 30BBA	247.1	497.2	217.8	108.7	163.3	300	180	3.3	1714.1	**44.7**
100RMA 30BBA	0	497.2	435.5	108.7	163.3	300	180	4	1684.7	**98.8**
Series 2										
75RMA 15BBA	247.1	609.5	321.9	72.5	86.1	300	180	3.4	1817.2	**43.9**
75RMA 55BBA	247.1	497.2	321.9	54.4	292.3	300	180	3.9	1892.9	**76.9**

Two types of series were elaborated. In the first set with a fixed amount of EC, there were two groups: the first group was created by replacing different percentages of coarse fraction natural aggregate by RMA and the second group was manufactured with the same percentages of RMA replacement and substitution of 30 % fine fraction of natural aggregate by BBA. Replacing NA by RMA and BBA has been performed in volume due to lower density which possesses recycled aggregates and biomass bottom ash respect to natural aggregates.

In the second set, a study was conducted by replacing NA and EC by RMA and BBA according to the size of particles. Two batches were made, the first with a replacement of 75 % of the coarse fraction of NA and EC by RMA and 15 % substitution of the fine fraction of NA and EC by BBA. In the second batch, the replacement percentage of the fine fraction was increased to 55 % of BBA.

The amount of cement used (300 kg/m^3) was kept constant in all concretes manufactured. With the objective of maintaining a similar consistency, the amount of additive was modified for each batch.

Materials were pre-saturated, as required by the regulations (EHE-08) [37]. his pre-saturation water compensates for increased water absorption possessing RMA respect to NA. The Bolomey method was applied to calculate the mixture proportions (Table 5.5).

A recycling factor was calculated to estimate the amount of recycled aggregate used in relation with the amount of natural aggregate. The value of this factor is 100 when the same amount of recycled aggregate and natural aggregate are used in lightweight concrete manufacturing.

The batch with a higher recycling factor corresponding to the 100 RMA/30 BBA where the same amount of recycled aggregate and natural aggregate is applied because the factor approaches 100 (Table 5.5). In series 2, the mix 75 RMA/55 BBA also presents a high recycling factor.

Manufacture of Concrete

The methodology used for the manufacture the mixtures was the same for all concretes. First, the coarse aggregate was introduced to the mixer, followed by the fine aggregate and 50 % of the total water. The mixture was homogenized for 5 min of mixing. Later, the cement and the additive dissolved in the remaining water were added and mixed for 5 min.

Finally, the specimens were manufactured and after 24 h the specimens were removed from their moulds. For the production of lightweight concrete, it was necessary to make a change in the vibration time relative to conventional concrete because a prolonged vibration caused the appearance of EC on the surface due to its low density. Then, the specimens were cured in the curing room at an ambient temperature of 20°C and 100 % relative humidity.

5.3.- Experimental Tests and Results

After exposure to the physical characterization, method of manufacture and experimental methodology, the experimental tests of lightweight concrete were cured, and results for all the properties analysed are shown here.

The experimental tests of hardened concrete are presented as follows.

Workability

The consistency of fresh concrete was measured by the slump in the Abrams cone (UNE-EN 12350-2).

Due to the incorporation of BBA as a substitute of fine fraction natural aggregates different amounts of superplasticiser were applied to obtain similar workability in all lightweight concrete manufactured (Table 5.6). All concretes showed similar consistency due to the realisation of previous studies of consistency.

Density and Absorption of Hardened Concrete

The density of hardened concrete is one of the more relevant characteristics, which must present lightweight concrete because its quality classifies this concrete as lightweight.

Density was measured at 28 days according to UNE EN-12390-7 in the reception conditions of curing in a moist chamber.

The apparent density of the lightweight concrete decreased as the natural aggregate replacement increased with the incorporation of RMA and/or BBA and was higher when the incorporation rate increased. Martínez-Lage et al. [3] obtained similar results: the density values of concrete decreased approximately 8 % with the incorporation of RMA.

In Series 2, an increase of density values was observed because a portion of EC (lower density value) was replaced by RMA and BBA. All density values are within the limits established in concrete Spanish Instruction (EHE-08) [37].

The density of hardened concrete is mainly dependant on the density of the aggregates used [38]. The reduction of density in lightweight concretes is due to the low density of the ceramic particles of RMA [39] and the high porosity of BBA [12]. Absorption significantly increased with the replacement of NA by RMA–BBA (Table 5.6). Moreover, absorption was higher with the increase of the replacement rate of NA by RMA–BBA.

Table 5.6: properties of hardened concrete

	AGE (Days)	CONTROL	50RMA 0BBA	100RMA 0BBA	0RMA 30BBA	50RMA 30BBA	100RMA 30BBA	75ARM 15BBA	75ARM 55BBA
Workability (mm)	0	8	9	8.5	8,5	8.5	8	8	9
Density (kg/dm^3)	28	1.8	1.75	1.66	1,69	1.64	1.57	1.79	1.81
Absorption (%)	28	8.8%	9.0%	12.5%	9.7%	11.1%	12.7%	10.9%	12.3%

This is inconsistent with Beltrán et al. [13], where significantly low density values in a concrete with replacement of BBA by the fine fraction of natural aggregates were obtained (an average of 6 % for 30 % BBA replacement).

As shown in Figure 5.3, a high correlation between the recycling factor and absorption exists in hardened lightweight concrete when NA was replaced with a blend of RMA–BBA.

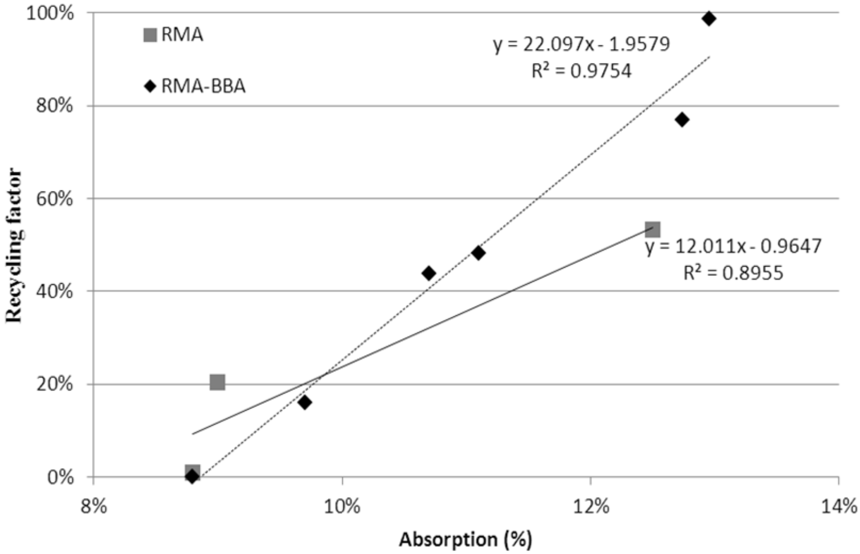

Figure 5.3: Correlation between recycling factor and absorption

Absorption of concrete and the addition of RMA are clearly correlated. This clearly demonstrates that the substitution rate of NA by BBA directly affects the absorption of concrete.

Compressive Strength

Compressive strength was determined according to UNE EN 12390-3. The property was determined at the ages of 1, 7, 28 and 90 days on cubic specimens with 100 mm sides.

A hydraulic press with a maximum capacity of 2000 KN was applied at a constant speed load.

For all ages, the control lightweight concrete obtained the highest values of compressive strength (Table 5.7). Compressive strength increased with curing age, as expected [38].

Table 5.7: Mechanical properties of hardened concrete

	AGE (Days)	CONTROL	50RMA 0BBA	100RMA 0BBA	0RMA 30BBA	50RMA 30BBA	100RMA 30BBA	75ARM 15BBA	75ARM 55BBA
Compressive strength (MPa)	1	13.4	16.5	13.4	13	15	12.7	15.1	9.1
	7	25.9	25.7	18.7	20.4	19.6	18.7	19.8	16.3
	28	31.6	30.1	23.7	28	26.7	21.3	27.1	20.4
	90	37.6	35	28.4	33.9	32.5	26.1	33.2	22.3
Flexural strength (MPa)	28	4.4	4.31	3.99	4.24	4.12	3.82	4.19	3.79
UPV (Km/s)	28	4.33	4.32	4.23	4.29	4.27	4.15	4.21	419

Other authors obtained similar values [8, 39]; approximately 75 % of the compressive strength at 28 days was obtained at only 7 days for the entire series.

The incorporation of the RMA and BBA caused a decrease of the compressive strength in relation to the lightweight concrete reference (CONTROL).

Despite the reduction in compressive strength, all lightweight concrete manufactured with recycled aggregates were within the limits established by the EHE legislation for structural and non-structural lightweight concrete (15–20 MPa).

The incorporation of the RMA caused average decreases of approximately 5– 25 % for replacement rates of NA by RMA of 50–100 %, respectively.

These results are between the values obtained by Martinez-Lage et al. [3] for 150 x 300-mm cylindrical specimens and Beltrán et al. [13] for 100 9 100-mm cubic specimens of conventional concrete at 28 days with the 23 and 27 % loss of compressive strength for a 100 % NG substitution of RMA, respectively.

Similarly, compressive strength decreased according to the BBA incorporation (Table 5.7; Figure 5.4). Concrete with 30 % BBA, without RMA, caused a decrease equal to 11 % of the compressive strength of the reference lightweight concrete.

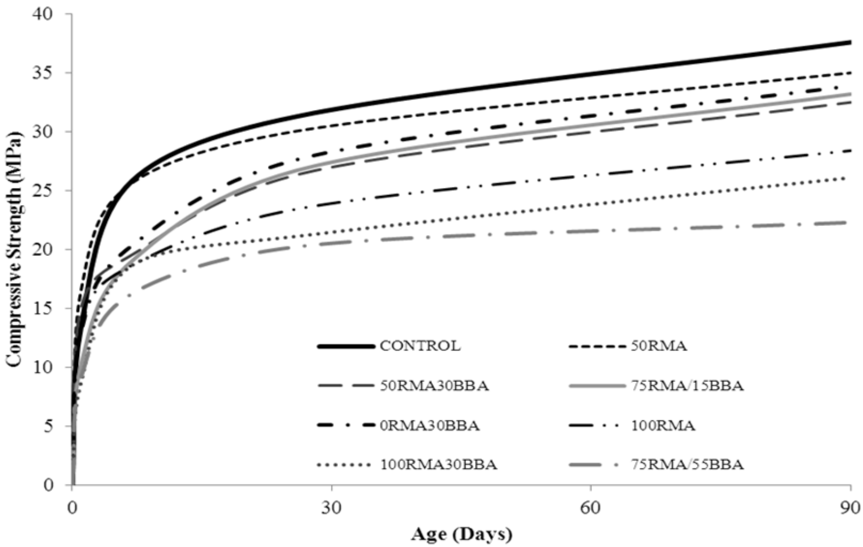

Figure 5.4: Evolution of compressive strength

The decrease of compressive strength depends on the type of aggregate, and it increases with the increase of density [39]. This fact was illustrated when low-density aggregates (RMA and BBA) were incorporated. This correlation presents clear values, as shown in Figure 5.5 when the fine fraction of NA was replaced by BBA for lightweight concrete manufacturing.

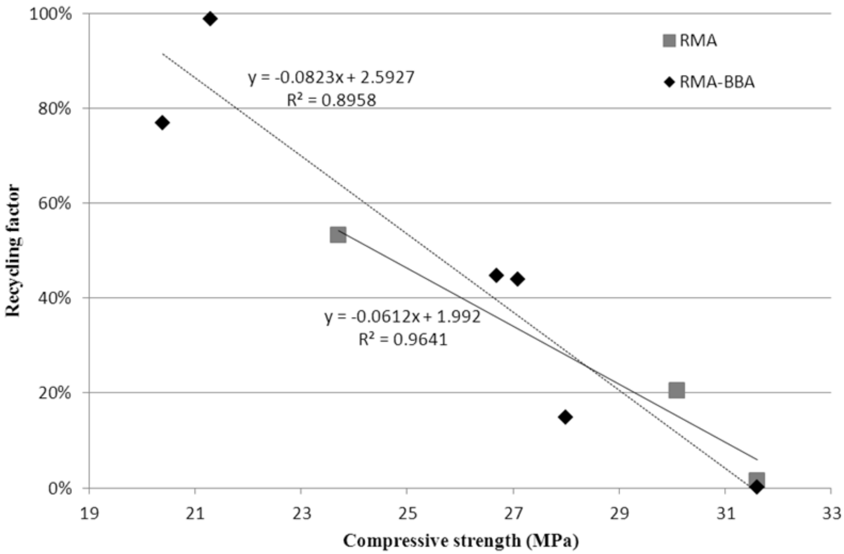

Figure 5.5: Correlation between the recycling factor and compressive strength

The incorporation of a blend of BBA and RMA showed a significant decrease of the compressive strength. Consequently, the recycled aggregates did influence the effect of BBA on the compressive strength, but the loss of compressive strength is not proportional to the amount of BBA and RMA incorporated, as was shown in RMA incorporation (Figure 5.5).

Flexural Strength

Flexural strength was determined using prismatic specimens with the dimensions of 100 x 100 x 400 mm3 cured for 28 days. This property was determined according to UNE EN 12390-5.

As for compressive strength, the flexural strength declined with the incorporation of RMA: 2–9 % for 50–100 % RMA incorporation, respectively (Table 5.7).

However, the decrease was less significant with respect to compressive strength.

BBA replacement in concrete with natural aggregate had effects similar to those of the incorporation of RMA (loss of 3 % for 30 %).

Conversely, lightweight concrete manufactured with RMA–BBA showed higher flexural strength losses.

Figure 5.6 shows the excellent correlation between the compressive strength and flexural strength for all concretes (R^2 = 0.99). Compressive strength can reliably determine the flexural strength for each concrete and vice versa. Other authors obtained a loss of strengths with the incorporation of RMA and BBA [17, 40].

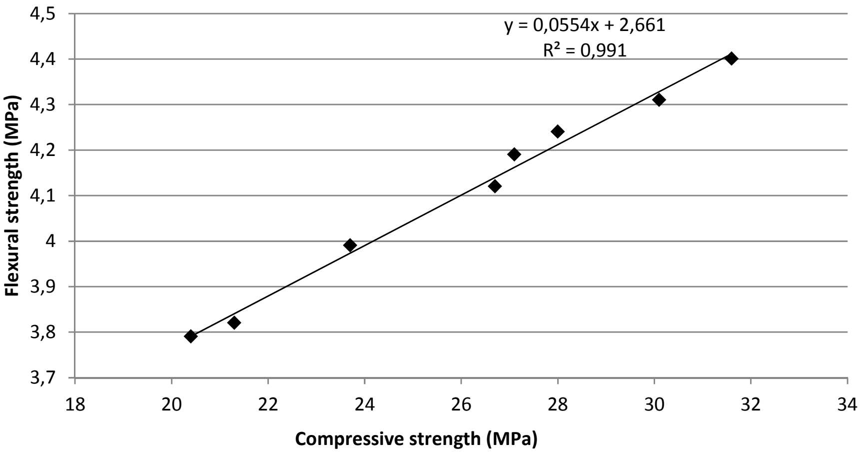

Figure 5.6: Correlation between compressive strength and flexural strength at 28 days

Ultrasonic Pulse Velocity

The ultrasonic pulse velocity (UPV) was obtained by direct transmission according to UNE EN 12504-4.

UPV increased with curing age due to a property related to the hardening of concrete (Figure 5.7), its strength and porosity. At 28 days of age, (CONTROL) obtained higher UPV. The values of UPV decreased with the replacement of NA by RMA and BBA (Table 5.7). Moreover, the reduction was higher with the increment of replacement rates.

Other authors obtained a reduction in UPV with the incorporation of RMA and BBA [13].

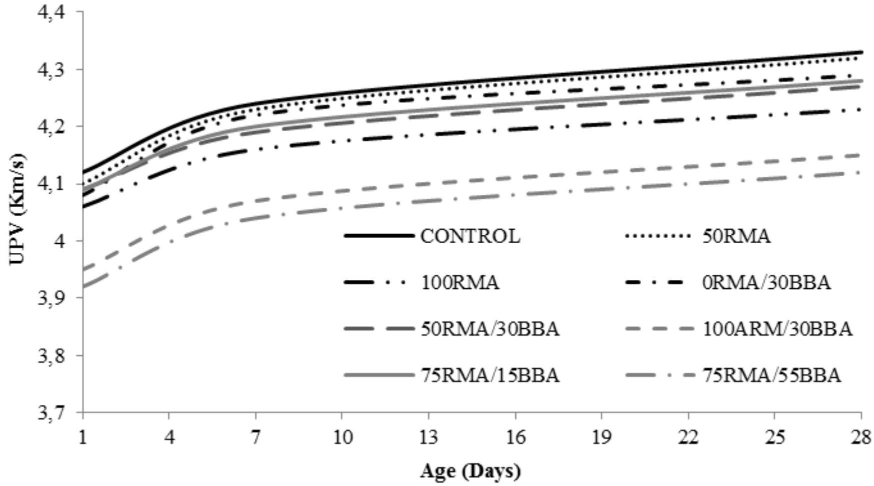

Figure 5.7: Evolution of UPV

The UPV test is a method that indirectly determines compressive strength [41]. The data analysed showed a correlation between both properties, which allows for obtaining the compressive strength from UPV with excellent accuracy (Figure 5.8).

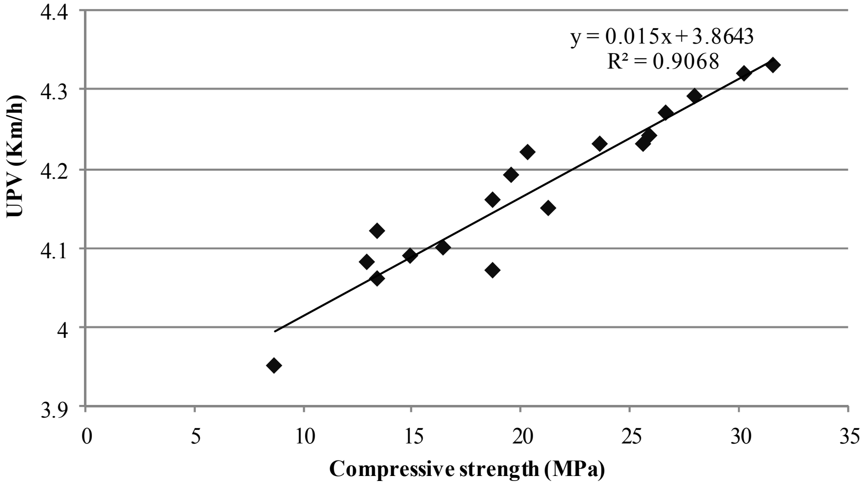

Figure 5.8: Correlation between compressive strength and UPV

A correlation between absorption and UPV was obtained due to absorption and UPV being properties related with the hardened concrete.

A higher correlation was observed for concrete manufacturing with RMA addition in relation to concrete manufacturing with combined BBA–RMA (Figure 5.9).

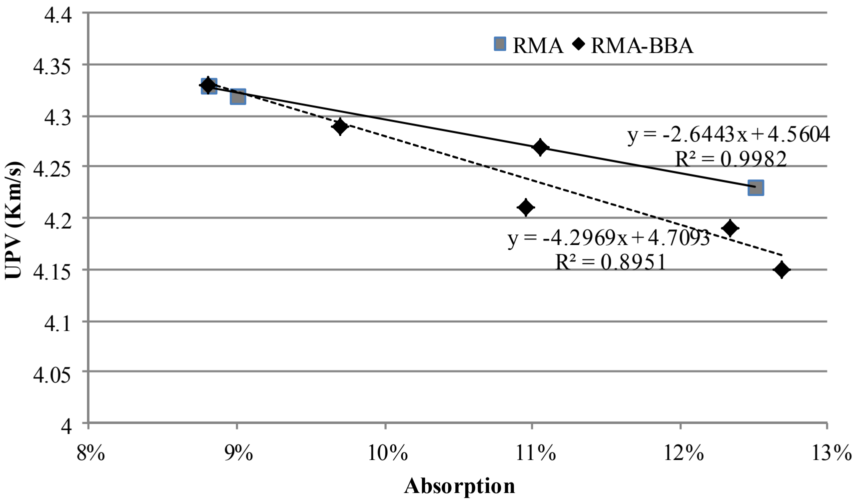

Figure 5.9: Correlation between absorption and UPV

Penetration of Water Under Pressure

The penetration of water under pressure was measured according to UNE-EN 12390-8 at 28 days. The penetration of water significantly increased with the replacement of NA by RMA–BBA (Table 5.8). This increase was more significant with the increment of the replacement rates of NA by RMA–BBA.

Table 5.8: Mechanical properties of hardened concrete

	AGE (Days)	CONTROL	50RMA 0BBA	100RMA 0BBA	0RMA 30BBA	50RMA 30BBA	100RMA 30BBA	75ARM 15BBA	75ARM 55BBA
Water Penetration (mm)	28	65.7	73.1	81.7	70.5	77.9	84.6	75.6	82.4
Shrinkage (µm/m)	90	434	479	501	448	485	524	4.67	531

Despite BBA presenting higher absorption values than RMA, the increase of the penetration of water rate in the blend of RMA–BBA was not significant compared to concretes manufactured with RMA. However, the recycling factor values (RMA and BBA) and water penetration are highly correlated among them (Figure 5.10).

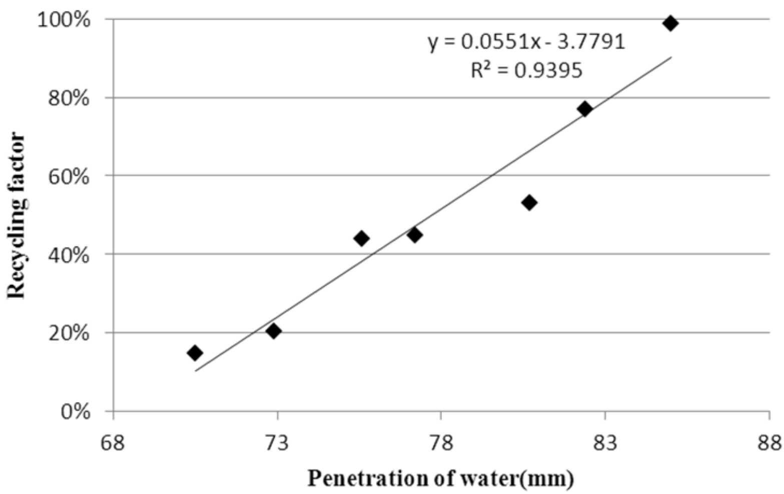

Figure 5.10: Correlation between the recycling factor and the penetration of water

Mas et al. [2] concluded that the penetration of water increased upon the addition of RMA. The increase was observed mainly due to the high porosity of these aggregates. However, other authors such as Martinez-Lage et al. [38] obtained less penetration of water when incorporating RMA.

Generally, penetration of water increases with the incorporation of RMA due to the higher porosity of its particles respect to NA. In addition, the high porosity of the particles of BBA contributes to increasing the water absorption and penetration of the hardened concrete [17].

Drying Shrinkage Test

To study the durability of the concrete, drying shrinkage measurements were obtained on concrete prisms measuring 100x100x400 mm according to ASTM C157. The specimens were exposed to conditions of 50 % relative humidity and 20°, and the measurements were taken for 1, 4, 7, 14, 28, 56 and 90 days.

The CONTROL concrete mixture presented less shrinkage respect to the recycled concretes. Higher values of shrinkage were obtained with the incorporation of RMA. Similarly, shrinkage values were increased with the incorporation of BBA, with the lower influence in concretes with respect to RMA. Concretes with a combination of RMA and BBA obtained higher values of shrinkage. The increase of shrinkage might be caused by the RMA and BBA particles, which provided water into the drying matrix at very early ages due to the high porosity of these materials [42].

Other authors obtained higher shrinkage in concrete with recycled aggregate additions [43–45]. Furthermore, 0 RMA/30 BBA also obtained higher shrinkage values, being equally evident at 90 days of age. However, in contrast to other properties, the influence of BBA was less significant than the influence of RMA, so for this property, RMA replacement presented more significant values (Figure 5.11, 5.12). At the same time, concretes manufactured with RMA–BBA obtained higher shrinkage values (Figure 5. 11).

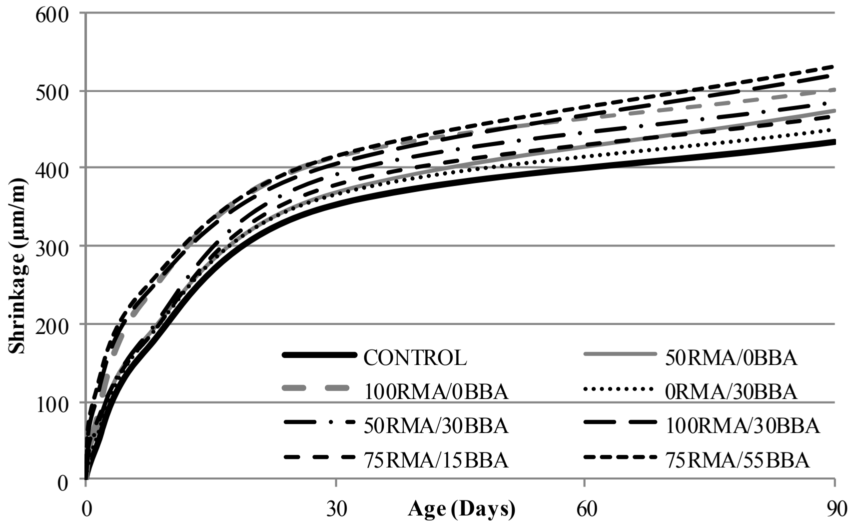

Figure 5.11: Evolution of drying shrinkage with respect to the reference concrete

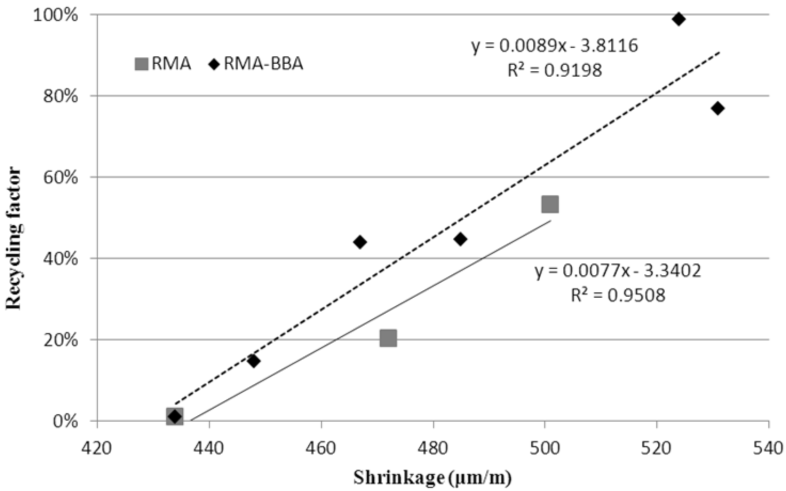

Figure 5.12: Correlation between the recycling factor and drying shrinkage

Furthermore, shrinkage of hardened concrete depends on multiple factors. A good correlation is obtained between water absorption and shrinkage, reflecting the importance of the absorption in this property (Figure 5.13).

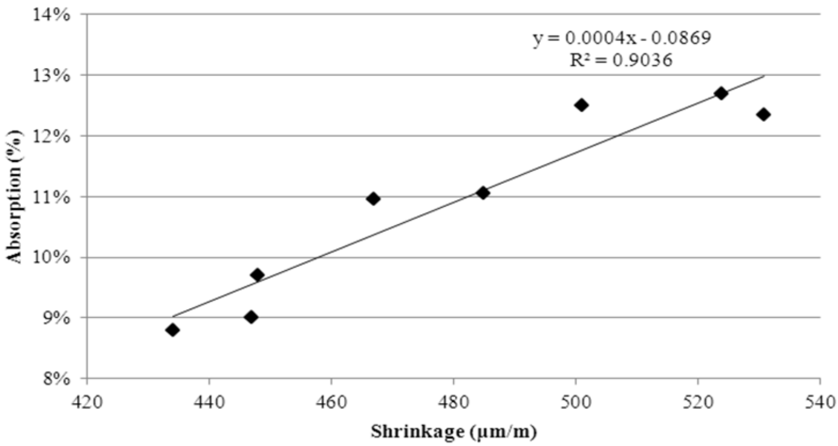

Figure 5.13: Correlation between absorption and drying shrinkage

5.4.- Conclusions

The following conclusions were obtained.

The incorporation of RMA and BBA allowed the acquisition of concrete mixtures with densities below 2 kg/dm^3 (LWC). Therefore, all replacements of NA by RMA/BBA can be applied for this type of concrete. Furthermore, RMA and BBA replacement did not improve the mechanical properties of lightweight concrete manufacturing due to the high content of ceramic particles and adhered mortar in the case of RMA and the high porosity and high organic matter content in the case of BBA.

However, despite the property loss in the lightweight concrete, the application of both types of materials can be performed individually or in a combination mix to reduce the replacement rates.

Although the mechanical properties of lightweight concrete with RMA and

BBA were reduced, these materials are within the limits established by the EHE-08 legislation, which establishes 15–20 MPa as the compressive strength value limit for structural lightweight concrete.

In summary, the replacement of expanded clay by RMA–BBA to manufacture recycled lightweight concrete is feasible; it presents a reduction of the properties of the mixtures and influences the mechanical and durability properties of the produced concrete, but the condition of lightweight concrete is achieved. Therefore, it is possible to use RMA and BBA with low replacement rates for lightweight concrete manufacturing that does not require high technical exigencies.

Thus, this study highlights the potential importance outputting a sub industrial product (BBA) and a waste (RMA). Structural lightweight concrete obtained complies with the specifications required by the rules and shows less density than a conventional one.

5.5.- Acknowledgments

The present work is a result of a project called ‘‘Study of the properties of recycled aggregate from CDW, RAP and BBA, to be applied in infrastructure works,’’ which was conducted in cooperation with the Sacyr Building company and University of Cordoba and was funded by the Ministry of Science and Innovation and the European Union through the ‘‘Operational Programme I + D + i and for the benefit of businesses (Technology Fund)’’ and the European Regional Development Fund (ERDF) within the INNPACTO 2011 programme.

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CAPÍTULO VI

FEASIBILITY USE OF OLIIVE BIOMASS BOTTOM ASH IN THE SUB-BASES ROADS ANS RURAL PATHS

Cabrera, M., Rosales, J., Ayuso, J., Estaire, J., & Agrela, F.

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VI

FEASIBILITY OF USING OLIVE BIOMASS BOTTOM ASH IN THE SUB-BASES OF ROADS AND RURAL PATHS

Cabrera, M., Rosales, J., Ayuso, J., Estaire, J., & Agrela, F. (2018). Feasibility of using olive biomass bottom ash in the sub-bases of roads and rural paths. Construction and Building Materials, 181, 266-275.

Abstract

Clay soils are widely distributed throughout the world and are the source of multiple technical problems in their application for the construction of sub-grade and sub-road bases. These types of soils are found in areas where civilian infrastructure such as roads and rural roads must be built. Therefore, in many situations it is necessary to use stabilized expansive soils, in the formation of the foundation and structural layers of linear infrastructures.

Soil stabilization is used to increase the load capacity of the soil, and mixtures of lime and cement are generally used as binders.

In recent years, interest in the recycling of industrial products and by-products has increased. One example of this is the use of biomass combustion in power plants. The management of significant amounts of waste (biomass bottom ash) from biomass power plants remains a problem.

This paper presents the results of an experimental study for stabilizing expansive soil to determine its bearing capacity and mechanical properties via a triaxial test of the addition of biomass bottom ash. A double objective was targeted: reduction of the problems in using this type of soil and provision of a use for this type of waste. The results showed significant improvements in the mechanical. Therefore, herein is proposed the use of biomass bottom ash as a stabilizing agent for expansive soils, to improve the efficiency of the construction process by incorporating this product into a second life cycle as road bases.

Keywords:

soil stabilization; biomass bottom ash; expansive soil; clay soils

6.1.- Introduction

In road and rural-path construction, it is essential to minimize the use of additional materials, and eliminate earth moving as much as possible, for environmental and technical considerations.

The soil treatment techniques contribute to the competitiveness and sustainability of road engineering [1]. The engineering properties of construction materials determine their potential use and application in civil works. The material characteristics must satisfy the engineering functions that contribute to the durability and quality of the entire road structure [2]. Previous works have proved the feasibility of reusing industrial residues from different origin which have been applied in road construction [3-4].

Soil stabilization is the process of alteration of geotechnical properties to satisfy engineering requirements [5]. Extensive studies have been carried out regarding the treatment of expansive soils using various additives, such as lime, cement, fly ash, industrial waste products, potassium nitrate, calcium chloride and phosphoric acid [6-13]. Traditional techniques of soil stabilization are often used to obtain geotechnical materials improved through the addition into soil of such cementing agents as Portland cement, lime, asphalt, etc. However, the traditional cementitious stabilizers like cement are under discussion, not only for their negative environmental effects during manufacture but also for their cost.

Those types of additives have been used in soils to improve their engineering properties, and to modify physical and chemical reactions with soil elements in the presence of water [14-18]. For this reason, this work seeks the feasibility of using new by-products with pozzolanic characteristics for use as a soil stabilizer. Based on previous studies in which fly ash is used as a stabilizer due to its high CaO content, hydrates forming cementitious pozzolanic products similar to those formed during the hydration of Portland cement or lime. [19-21]. This research demonstrated the possibility of removing cement as a stabilizing material, replacing it with ash from the combustion of biomass for the generation of energy in combination with lime.

In addition to cement, lime is one of the most used materials for soil treatment. Lime is a very caustic, pure white substance that results from the calcination of limestone. The common lime is calcium oxide CaO, also known as quicklime, which is widely used in construction.

Lime can usually be obtained via thermal decomposition of materials such as limestone, which contains calcium carbonate ($CaCO_3$), extracted from sedimentary deposits called caliche. It is subjected to very high temperatures (900–1200 ° C), for a period of three days in a rotary kiln or in a special furnace called a lime kiln. However, if not managed, the process is reversible: while cooling, the lime begins to absorb CO_2 from the air again; after a while, it once again becomes $CaCO_3$ (calcium carbonate).

The long-term operation of any construction project depends on the quality of the underlying soils. Unstable soils can create significant problems in built structures and pavements. With appropriate design and construction techniques, unstable soils can be chemically transformed into usable materials. In addition, the structural support provided by lime- or cement-stabilized soil can be exploited in pavement design.

In general, the good results obtained from treatment with lime or cement, as applied in the construction of roads and esplanades, have extended this technique to any type of geotechnical problem and to esplanades with low bearing capacity [22]. The use of stabilized or treated soils, even with marginal and contaminated soils, avoids the reduction of natural resources by reducing the need for better quality soil. Moreover, clearance operations and transportation to a landfill are avoided, along with the extraction and transportation work conducted to replace the soil. It is a technique clearly focused on achieving greater sustainability.

One of the biggest drawbacks of stabilization using lime or cement is their small particle size. Dust can be a problem, and its management is generally inadequate in populated areas. In addition to the high volumetric weight of such additives, which makes them more expensive to transfer, the dosage is altered in places where it is very windy. Moreover, the hydration process is more expensive when done in a plant rather than doing it at the site of application.

Biomass is a term with many definitions. For the purposes of this paper, biomass is considered as any organic (non-fossil) material burned as fuel to generate electricity or produce heat.

Biomass-based products produce solid residue (ash) a result of thermochemical degradation. Thermochemical processes include combustion, pyrolysis, and incineration of woody biomass.

Currently, research is being conducted regarding the use of biomass ashes for civil works. In Spain, Andalusia leads in its scope of power generation from biomass, with 18 biomass combustion plants and a total installed capacity of 257.48 MW [23, 24]. The waste biomass in Andalusia from grapevines, olives, fruit trees, and poplar, is used as a source of renewable, sustainable energy to provide heat in homes. Biomass ashes are the solid by-products that remain after complete or incomplete combustion of organic matter. Industrial biomass ashes consist of biomass bottom ash (BBA), or slag, and biomass fly ash (BFA).

BBA and BFA have been extensively studied, with focus on several applications. BFA has typically been used in agriculture due to its nutrient mineral content, including calcium, potassium and phosphorus [25]. Because of the increased production of this by-product, BFA has been investigated regarding its use in building materials. While fly ash utilization has been extensively studied, similar studies on the effective management and utilization of bottom ash have been scarce. BBA is traditionally disposed of in landfills.

In recent studies, biomass bottom ash from wood combustion and agricultural olive residues was used as filler material in road embankments, as well as in the manufacture of cement-treated recycled materials and as additive in the manufacture of lightweight recycled concrete [26-28].

Therefore, it would be interesting to study the possible application of bottom ash biomass for soil stabilization or treatment, and more specifically, for its use in the region of Andalusia in southern Spain. This region has problems related to expansive soils and has an abundance of European combustion power plants as well as higher concentrations of available biomass.

The goal of the present work was to evaluate the possibility of using BBA as a soil treatment to stabilize the sub-bases of roads and rural paths according to the technical specifications for road works imposed by Spanish regulation [29].

This article discusses the experimental results of improvement of the properties of an expansive soil when it is treated with biomass bottom ash.

Thus, the treatment or stabilization of expansive soils has been considered from the standpoint of civil engineering. These experiments have been based on tests to evaluate the use of these types of soil as building materials.

To these ends, the following parameters were measured to physically and mechanically characterise the samples: granulometric composition, absorption, density, compactability according to the modified Proctor test, bearing capacity based on the CBR index, plasticity and the triaxial compression test, x-ray fluorescence spectrometry and scanning electron microscopy analysis with x-ray spectroscopy.

The potential for using BBA mixed with clays at certain percentages of dosage. This BBA valorisation could avoid a large amount of the waste currently being sent to landfills, providing economic and environmental incentives.

6.2.- Materials and methods

Biomass bottom ashes (BBA)

In this work Olive Biomass Bottom Ash (BBA) was studied and applied in the formation of granular materials to be applied in road structural layers.

Based on the data, a power plant burned approximately 40% olive cake and 60% wood biomass (poplar, olive and pine).

The biomass sample analysed in this study was collected after combustion at the plant BioLinares, as characterized in specific studies performed previously [26, 30]. A summary of the physical and chemical characterization of this sample material is shown in Table 6.1.

Table 6.1: Summary of the main physical and chemical properties

	Particle size distribution (%)		Specific density of the solid particles **(g/cm^3)**	Water absorption **(%)**	Chemical compounds **(%)**		Organic matter content **(%)**	Loss on ignition **(%)**	Total sulphur content **(%SO^3)**
	UNE-EN 933-2		UNE-EN 1097-01		UNE 80-215		UNE 103204		EN-1744-1
	10 mm	97.0			Si	25.14			
	8 mm	95.1			Ca	16.78			
	4 mm	84.8			K	14.28			
	2 mm	65.2			Mg	3.09			
BBA			2.46	20.11			4.89	15.50	0.39
	1 mm	39.0			Fe	1.64			
	0.5 mm	23.1			Al	0.76			
	0.25 mm	13.1			Na	0.35			
	0.063mm	5.40			Ti	0.12			

According to the results, BBA is composed of extremely porous particles with rough surface textures. The size of these particles varies from sand to fine gravel. The water absorption and saturated surface-particle density were measured. Absorption is an important factor to consider because many physical parameters of bottom ash are altered in the presence of excess water [31, 32]. Low dry-surface particle densities (SSD) were calculated for the BBA sample. Compared to traditional natural aggregates, low densities were obtained for BBA because it is composed of particles with low specific weight [33, 34]. The chemical composition of BBA indicated that BBA primarily consists of Si, Ca and K, while the measured amounts of Mg, Fe, Al, Na and Ti (minor elements) were < 5%. Thus, Si is the most abundant element, followed by Ca and K (in similar amounts). Due to the nature of the material, the BBA sample tested contained 4.89% organic matter.

The X-Ray Diffraction Analysis (XRD) of the BBA (Figure 6.1) shows that the most representative phase of the bottom ash is quartz, which is typically produced at high temperatures during the combustion process. There is also significant presence of the crystalline phases of calcite, because biomass fuel contains a naturally high content of wood waste.

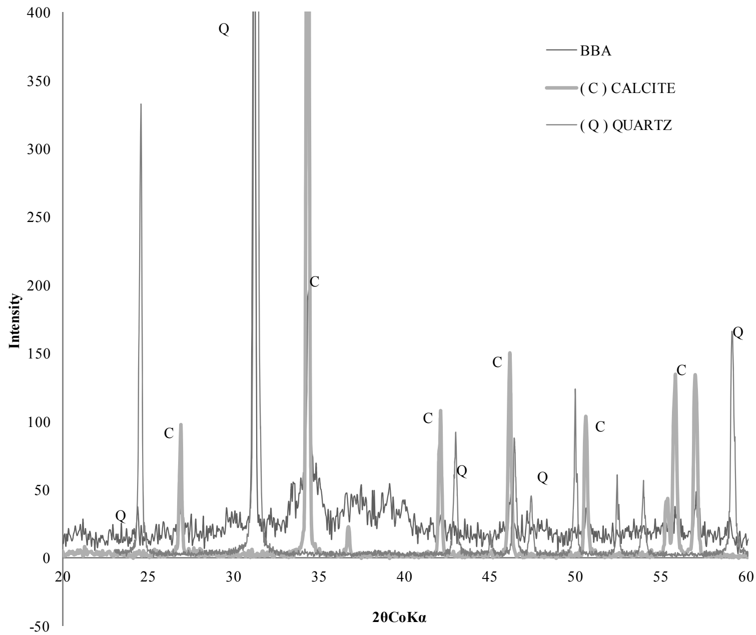

Figure 6.1: X-ray diffractogram of BBA

Quicklime

Hydrated lime is obtained when quicklime reacts chemically with water. Hydrated lime (calcium hydroxide) reacts with clay particles and permanently transforms them into a strong cementitious matrix. The plasticity and chemical properties are summarized in Table 6.2.

Expansive clay soil (ECS)

Expansive soils are those which show volumetric changes in response to changes in their moisture content. Such soils swell when the moisture content is increased and shrink when the moisture content is decreased. Consequently, expansive soils cause distress and damage to structures founded on them.

The expansive clay soil analysed was stockpiled on the premises of the University of Córdoba. The maximum aggregate size was 2 mm. Chemical analysis highlighting the elemental content of elements (Table 6.2) and the organic matter content was 1.20 wt%, as determined according to standard UNE103 204.1993.

Table 6.2: Physical and chemical properties

		Quicklime	ECS
Liquid limit (UNE 103-103-94)		-	59.2
Plastic limit (UNE 103-104-93)		-	39.9
Plasticity (LL-PL)		-	26.3
Organic matter (%) (UNE 103-204)		-	1.2
Elemental content (%) (UNE 80-215)	Si	<0.01	23.48
	Ca	52.9	16.8
	K	<0.01	0.74
	Mg	0.15	1.17
	Fe	0.03	2.93
	Al	0.03	3.44
	Na	0.02	0.23
	Ti	<0.01	0.45

Figure 6.2 shows the size distribution of the swelling clays. As a clay material, with much of the sample tested, 95% were among the fractions below 0.063 mm.

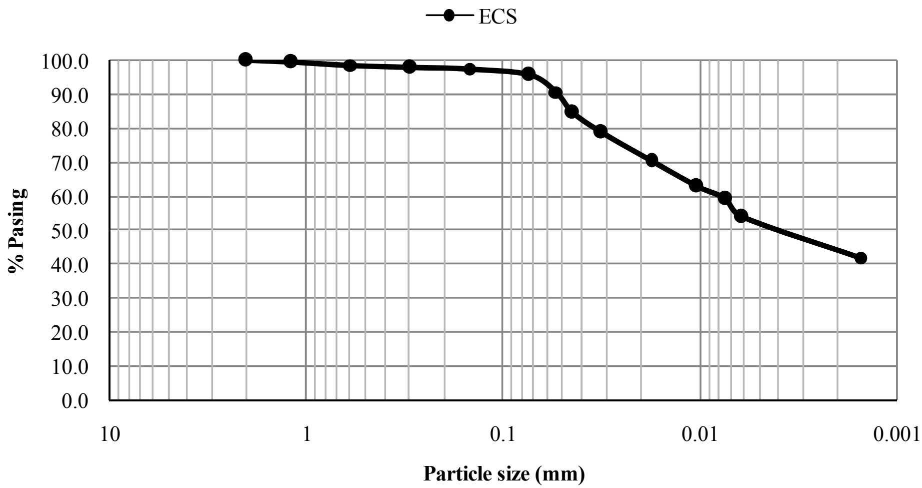

Figure 6.2: Particle size distribution curves

Mixtures

In this study, four different percentages of BBA were added to the expansive material, 0, 15, 50 and 100%; furthermore, the expansive material was mixed with 5 wt% quicklime. Table 6.3 shows the mixes obtained in the laboratory as well as the name used for the different mixes.

Table 6.3: Dosages of the mixtures

Nomenclature	ECS	BBA	Quicklime
ECS	100%		
BBA		100%	
ECS+BBA(50/50)	50%	50%	
ECS+BBA(85/15)	85%	15%	
ECS+5% QL	95%		5%

Methods

a) Modified Proctor

The Modified Proctor compaction test is a laboratory geotechnical testing method used to determine soil compaction properties, specifically, to determine the optimal water content at which soil can reach its maximum dry density.

The Modified Proctor compaction test, in accordance with UNE 103-501-94, consists of compacting soil samples with given water content in a standard mould with standard compaction energy. The procedure specifies a hammer weighing 4.5 kg and a freefall distance of 457 mm. All the materials were compacted in five layers, applying 60 blows to every layer.

b) California bearing ratio (CBR)

This test method is used to evaluate the potential strength of sub-grade, sub-base and base course material, including recycled materials for use in road and airfield pavements. The CBR value obtained in this test forms an integral part of several flexible pavement design methods.

This test is performed according to UNE 103 502-95, which describes the process for determining the resistance index of soils called CBR. This index is not an intrinsic material value but depends on the conditions of density and soil moisture, as well as the overload to be applied while performing the test.

This study was conducted with 25% Modified Proctor (MP), 50% MP and 100% MP value tests and an overload of 4.5 kg. The evolution of the tested specimens was examined under different external conditions and over time. The four test conditions were un-soaked CBR, 4-day soaked CBR, 90-day soaked CBR and 90-day in dry chamber CBR. The dry chamber had a temperature of 20 °C and 72% humidity.

c) Triaxial compression test

The Triaxial Compression Test is a laboratory test method used to assess the mechanical properties of rocks and fine-grained soils. It provides a measure of the confined compressive strength and the stress-strain characteristics of rock, soil or other material specimens. It is most often applied to soil and rock samples to simulate in situ confining pressures and to measure the corresponding strength and deformation characteristics. Triaxial compression tests performed over a range of confining pressures are used to define a material's strength envelope.

The specimen (either rock or reconstituted soil) is encased by a thin rubber membrane and placed inside a pressure vessel. The pressure vessel allows the specimen to be loaded hydrostatically to the desired confining pressure, while the rubber membrane prevents confining fluid from contaminating the sample. In a conventional triaxial compression test, the specimen is first loaded hydrostatically to the desired confining pressure and then the axial load is increased to specimen failure while holding the confining pressure constant. The applied load and resulting deformation was measured using our data acquisition system to generate load-deformation curves. The sample was loaded until it:

- Exceeded its confined compressive strength (brittle failure), or

- Reached 15% axial strain.

At sufficiently high confining pressures, the soils reach a brittle-ductile transition. Above this stress state, the material may continue to increase its load carrying capability without apparent failure as additional axial strain is imposed. In this case, the state of stress at an axial strain of 15% is conventionally used to define the strength envelope. For porous samples, a pore pressure can also be applied through a small hole beneath the specimen to simulate in situ conditions.

The triaxial test is performed according to UNE 103 402-98, which determines the strength parameters of a material sample in CU test mode: consolidated and undrained, with a pore pressure measurement assay. The specimen is saturated, consolidated under isotropic conditions and the test proceeds until compressive failure.

d) Free-swelling

A series of free-swell tests were conducted on specimens compacted with optimum water content and to a density equivalent to 100% of standard Proctor compaction. The apparatus used for free-swell testing was an odometer, according to UNE EN 103 601-96. The free swell is the increase in height (expressed in percent) when a specimen is laterally confined, subjected to a vertical pressure of 10 kPa and then flooded.

The soil specimen was placed in a fixed-ring consolidation cell, and the specimen was subjected to a confining pressure. During testing, vertical movements of the specimen were monitored using a dial gauge and a linear variable differential transducer.

After the specimen was placed in the apparatus and the seating load was applied, the height of the specimen was monitored. Once the height of the specimen came to equilibrium, data were logged from the linear variable differential transducer and water was added to the reservoir in which the soil specimen was sitting to begin swell testing the specimen.

A total of five tests were made in parallel in the laboratory to evaluate the free-swell characteristics of all mixtures.

e) X-ray fluorescence spectrometry (EDXRF)

The elemental concentrations were determined using energy dispersive an X-ray Fluorescence (EDXRF) Spectrometer according to UNE EN 196-2. EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in soil samples. Quantitative x-ray fluorescence data were collected using Panalytical NHM-X226 and quantified using Super Q software. The samples were fused and analysed by the Rietveld method.

f) Scanning electron microscopy analysis with x-ray spectroscopy

Analysis by Scanning Electron Microscopy (SEM analysis or SEM microscopy) was used for solid material characterisation. SEM facilitates the study of particles and surfaces with the added benefit of acquiring elemental composition for the sample being studied

6.3.- Results and discussion

a) Modified Proctor

Figure 6.3 shows the graphical representation of the results of the Modified Proctor test, it is possible to observe that all the materials presented curves very insensitive to changes of moisture content, making it necessary to ensure that the moisture content was close to the optimum value during compaction.

As expected, with the ECS+BBA mixture, the moisture and density values obtained were intermediate compared to those of the pure unmixed materials, highlighting the high humidity of these materials to achieve relatively low densities. In previous research [26], these results were confirmed for BBA. The plane curves shown indicate that these materials do not exhibit high sensitivity to changes in moisture for compaction.

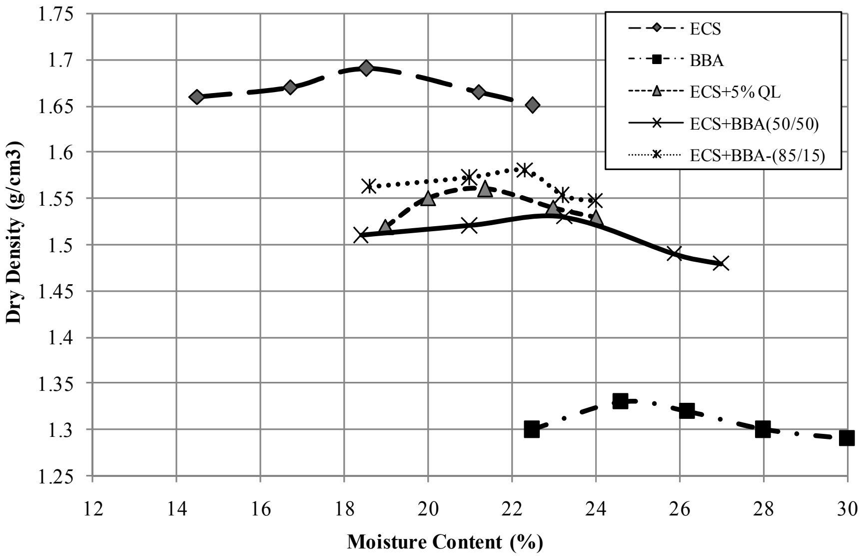

Figure 6.3: Moisture-density relationships

b) California bearing ratio (CBR)

Table 6.4 shows the results obtained from the CBR tests for the four modalities selected for these tests and for the materials studied, and Figure 6.4 shows graphs of the CBR values obtained for 100% MP in the four modes in which the tests were performed. For the 90-day soaked and 90-day dry chamber tests, the value represented is the average of three samples.

Table 6.4: CBR values

	Un-soaked CBR			4-days soaked CBR			90-days soaked CBR	90-days dry chamber CBR
	25% MP	50% MP	100% MP	25% MP	50% MP	100%	100% MP	100% MP
ECS	3.24	8.15	13.05	1.2	1.4	2.3	1.31	58.89
BBA	13.96	21.53	35.09	11.66	17.62	28.01	38.69	44.98
ECS+5% QL	8.12	14.62	22.31	2.24	3.58	4.67	36.81	69.19
	15.64	22.89	25.84	12.45	23.11	33.70	41.71	63.64
ECS+BBA	10.89	18.22	21.39	6.48	15.22	19.75	30.55	54.31

Comparing the values in the four test modalities it is observed that all ECS + BBA mixtures improved soil bearing capacity. The value compared to ECS was increased by 98% for ECS + BBA (50/50) and by 64% for ECS + BBA (85/15) when un-soaked. The measured values in BBA are consistent with the data obtained by previous authors [35], who characterized bottom ashes to be applied in civil infrastructures.

Previous research used ash from different byproducts such as Rice Husk Ash [36], Palm Oil Fuel Ash [37], 'Bagasse Ash' from sugar industry [38]. In all the researches the use of these ashes decreased CBR values (fundamental property of stabilized soil) or it has been necessary the use of cement to obtain acceptable conditions of stabilized soil. However, this new research demonstrates the high pozzolanic capacity of BBA due to its chemical composition and the viability of use as a stabilizing material.

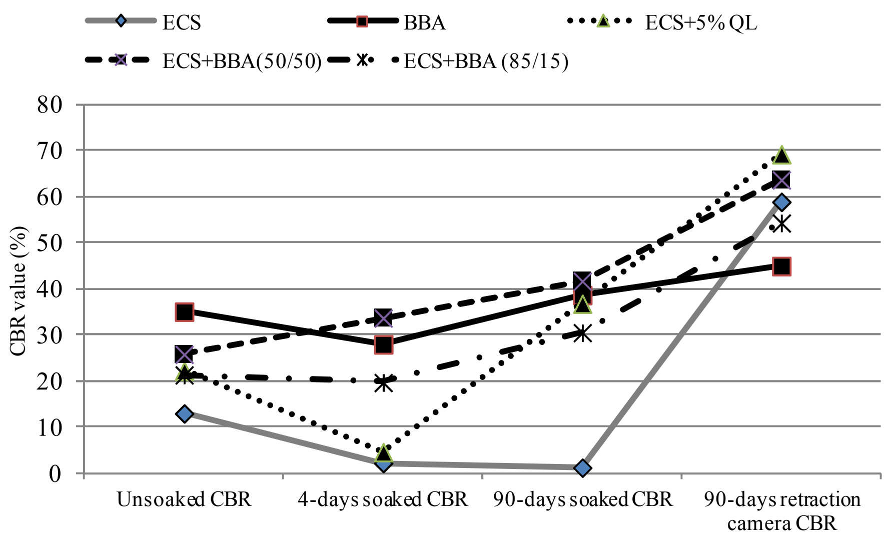

Figure 6.4: CBR values in 100% MP in different CBR tests

c) Triaxial compression test

Five CU triaxial tests were conducted using the different materials analysed in this paper. The conditions of sample preparation are shown in Table 6.5.

Table 6.5: Conditions of sample preparation

Material	Water content (%)	98% MP (Dry Density)	Confining pressures (kPa)
ECS	18.54	1.66	650 - 750 - 850
BBA	24.66	1.30	650 - 750 - 850
ECS + BBA (50/50)	23.27	1.50	650 - 750 - 850
ECS + BBA (85/15)	22.32	1.55	650 - 750 - 850

The curves of axial deformation-deviatoric stress obtained in the tests can be observed in Figures 6.5, 6.6 and 6.7.

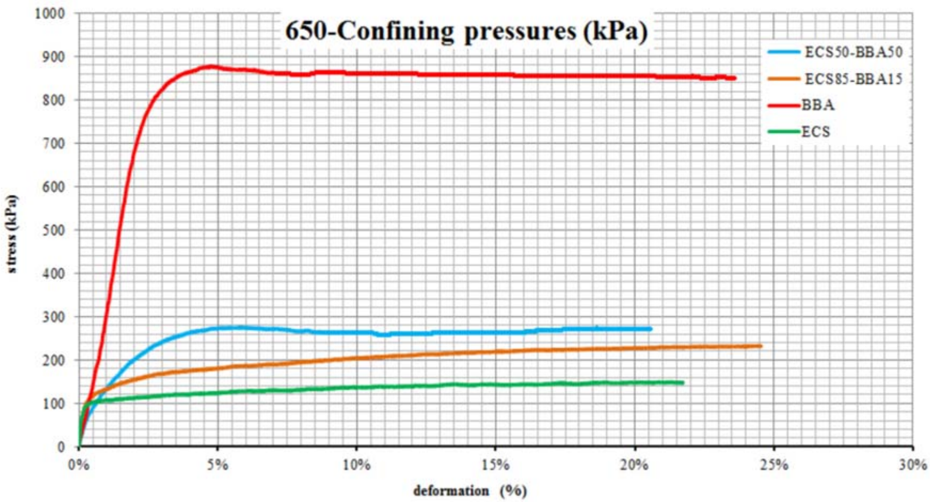

Figure 6.5: Stress-strain curves: Tests performed with 650 (Kpa) confining pressures

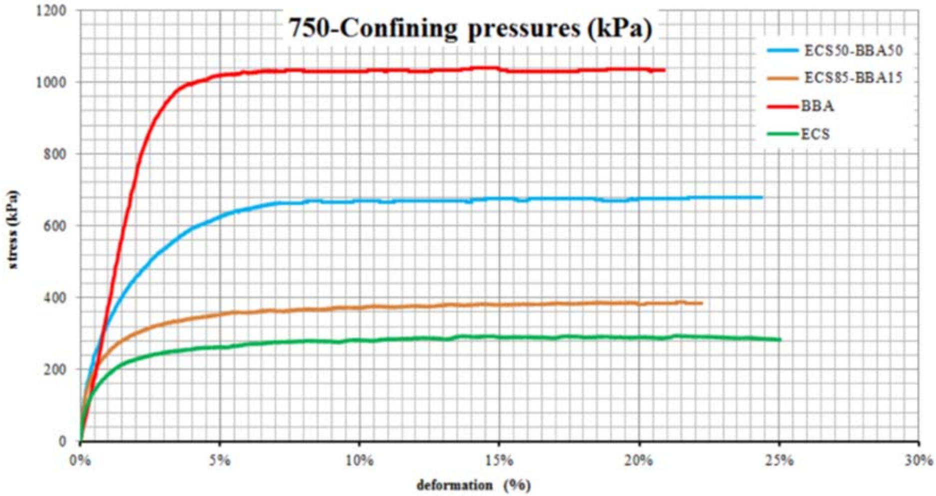

Figure 6.6: Stress-strain curves: Tests performed with 750 (Kpa) confining pressures

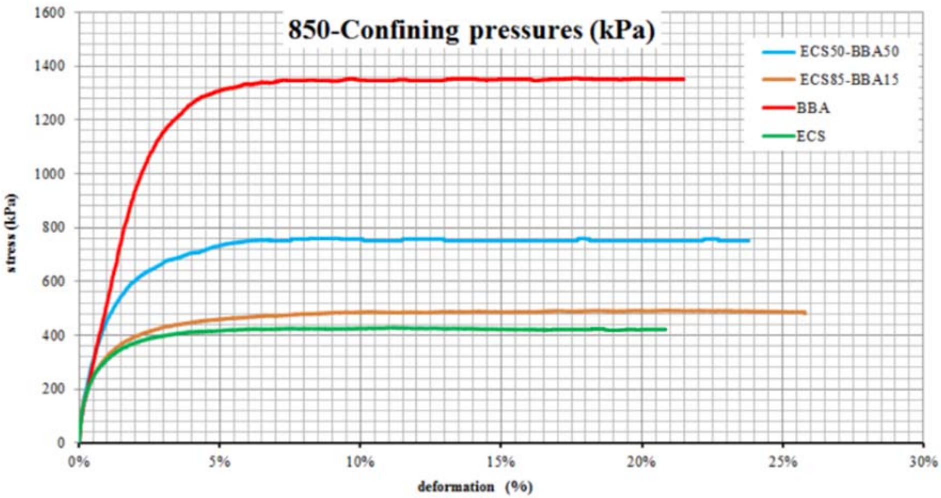

Figure 6.7: Stress-strain curves: Tests performed with 850 (Kpa) confining pressures

A uniform mass of expansive soil which becomes saturated with moisture will exert pressure in all directions as each individual expanding clay mineral seeks to occupy more space. The direction and magnitude of soil movement will depend upon the magnitude of the confining pressure at any particular point of resistance. Soil movement will be minimized where confining pressures are largest, while movement will be greatest where the magnitude of the confining pressure is smallest.

The analysis of the stress-strain curves obtained in the triaxial tests makes it possible to highlight the following aspects.

In the tests conducted with BBA, the deviatoric stress obtained was much greater than that obtained with ECS.

Once BBA was mixed with ECS in the proportion 50:50 wt%, the deviatoric stress was reduced by approximately 55% with respect to the values obtained with BBA.

The mixing of ECS with BBA produced a deviatoric stress approximately 35% of the value obtained with BBA.

The interpretation of those curves allowed us to calculate Mohr-Coulomb parameters with the aid of the s´-t diagrams, as seen in Figure 6.8.

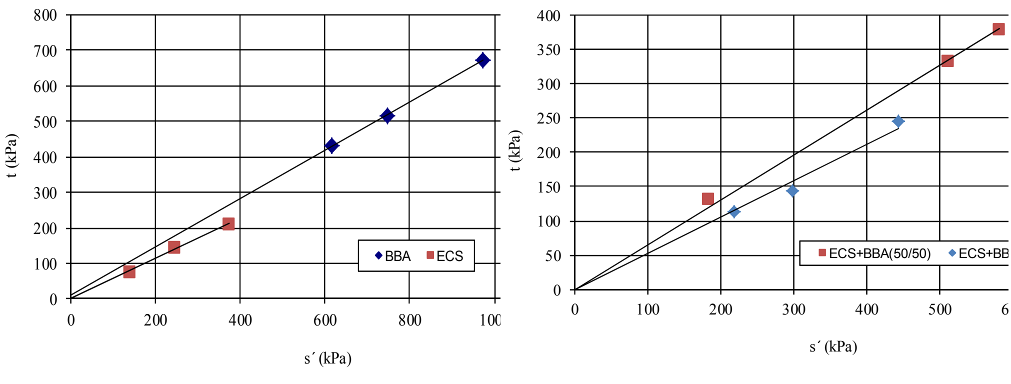

Figure 6.8: Tests performed with ECS and BBA (Left) and tests performed with ECS + BBA (50/50) and ECS + BBA (85/15) (Right).

It can be observed that the relevant points fit very well on lines that can be interpreted as representative of the Mohr-Coulomb failure criteria. The values of friction angle obtained with these tests are summarized in Table 6.6.

Table 6.6: Triaxial strength parameter values

	Strength Parameters (Effective)
	Φ'
ECS	34.6
BBA	43.7
ECS+5% QL	27.5
ECS+BBA (50/50)	40.7
ECS+BBA (85/15)	31.9

Table 6.6 shows the values of the Mohr-Coulomb failure criteria obtained in the tests.

All the materials seem to exhibit non-cohesive behaviour. ECS has a friction angle of 35° (a bit large for its clayish nature) that increases to 41° once mixed with 50% BBA. The mix of 85% ECS with 15% BBA seems to have strength similar to that of the original ECS.

From this point of view, the strength of all of these materials, and their combinations, can be considered high and sufficient to build any type of embankment.

d) Free-swelling

Furthermore, upon completion of the CBR tests (Section 5.3.b), the expansivity swelling values of each material (expressed in percent) were obtained. Table 6.7 shows the results obtained for the various swelling tests conducted.

Table 6.7: Swelling test values at four days

	% Free-Swelling	*% Swelling CBR*
ECS	6.74	2.95
BBA	0.06	0.01
ECS+5% QL	0.02	0.05
ECS+BBA (50/50)	0.04	0.13
ECS+BBA (85/15)	0.18	1.30

As shown in Table 6.7, the ECS sample showed a high percentage of free swelling. When the ECS was mixed with 50% bottom ash from the biomass (i.e. ECS + BBA at 50/50), the free swelling was reduced by 99.5%. This reduction was similar to that achieved with the mixture manufactured with 5% lime (ECS QL + 5%).

Regarding CBR swelling, the behaviour patterns were similar to those shown for free swelling. It can be concluded that the use of BBA reduces the expansion of expansive soils to the same extent (percentage) as lime. This demonstrates economic and environmental benefits from using this industrial by-product in this way.

e) X-ray fluorescence spectrometry (EDXRF)

Using Quantitative X-ray Fluorescence Analysis, the different types of experimental materials and processes were analysed to compare their predominant elements, shown in Table 6.8.

Table 6.8: Oxide composition by EDXRF Analysis

	H_2O	P.F.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	CaO free
					(%)					
ECS	1.20	19.77	43.01	8.90	2.95	20.97	1.50	0.20	1.69	0.02
BBA	4.25	17.95	39.63	4.48	1.89	20.92	2.65	0.46	8.97	1.62
ECS+BBA (50/50)	2.84	18.33	43.73	6.96	2.45	20.63	2.03	0.22	5.33	0.76
ECS+BBA (85/15)	1.75	19.42	44.15	8.62	2.83	20.79	1.70	0.16	2.72	0.27
ECS+5% QL	3.93	17.64	42.08	11.20	4.18	17.77	3.08	1.48	1.96	1.45

According to the results, this BBA contains a mixture typical of olive waste ash, but with higher values of potassium (8.97%). Also, the increase of lime in BBA, as shown in Table 6.8, can lead to increased pozzolanic activity [39].

f) Scanning electron microscopy analysis with x-ray spectroscopy

By this procedure the signals generated during the analysis produce two-dimensional images which reveal information about the tested samples (see charts in Figure 6.9 including external morphology: texture). The present study also includes the composition of samples as estimated by x-ray spectroscopy.

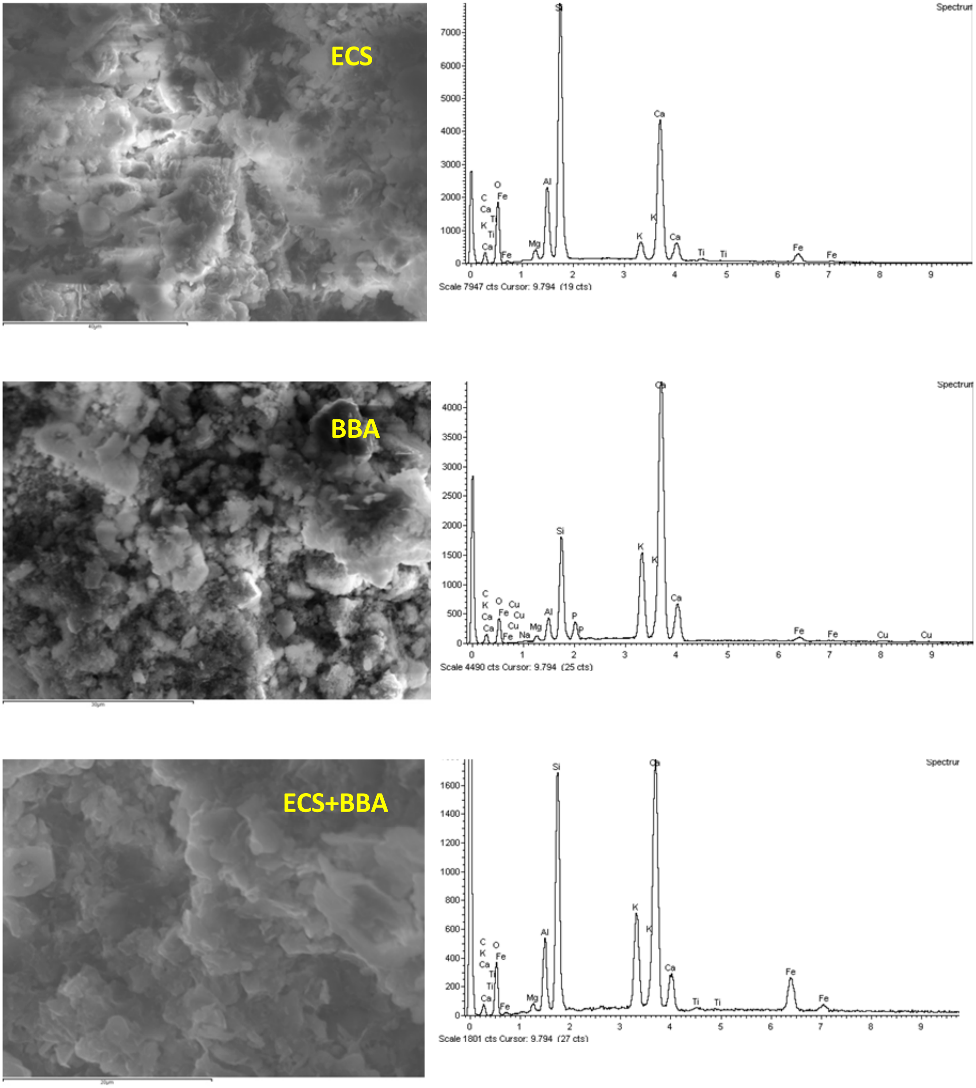

Figure 6.9: Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

The microstructure of samples was characterized using SEM. In Figure 6.9, it was observed that the BBA particles were irregular in shape. The ECS particle size was typically < 63 µm and in agreement with the particle size analysis results.

The expansion potential of any particular expansive soil is determined by the percentage of clay and the type of clay in the soil. The clay particles which cause a soil to be expansive are extremely small. Their shape is determined by the arrangement of their constituent atoms, which form thin clay crystals.

According to EDX analysis with the SEM, the clays belong to a family of minerals called silicates. The principal elements in the clay were silicone, aluminium and oxygen; whereas the major elements in the BBA were Ca, K, Si and Al (Table 6.9).

Table 6.9: Percentage weight of elements

Element	Weight %		
	ECS	BBA	ECS+BBA(50/50)
C	11.43	9.28	6.51
O	39.05	26.72	31.24
Na	0	0.22	0
Mg	0.89	0.57	0.62
Al	5.22	1.91	4.3
Si	20.4	8.85	15
P	0	1.96	0
K	1.97	10.24	8.13
Ca	17.9	38.06	24.98
Ti	0.29	0	0.39
Fe	2.84	1.51	8.83
Cu	0	0.67	0

6.4.- Conclusions

Based on the results obtained, we present the following conclusions:

- The addition of BBA in all the mixtures improved the bearing capacity, mainly due to the high calcium content that increased the pozzolanic activity.
- When the ECS was mixed with 50% bottom ash from biomass, the free swelling was reduced by 99.5%. This result is similar to those reported for the mix with 5% lime.
- The flat curves obtained by the modified Proctor test confirm that BBA do not exhibit high sensitivity to changes in moisture for compaction.
- Regarding the values of Mohr-Coulomb failure criteria obtained in the tests, the strength of all of these materials (and their combinations) can be considered high and sufficient to build any type of embankment.
- It can be concluded that the use of bottom ash from biomass combustion reduces the expansion of expansive soils to the same extent as from treatment with lime.

The present work has proved, at least for certain dose percentages, the benefits of BBA for improved mechanical ability and stabilization when used for material construction in civil infrastructure. The valorisation of this product, instead of exploiting natural resources or non-renewable natural resources, can eliminate the negative impact associated with the indiscriminate disposal of this by-product in landfills.

6.5- Acknowledgments

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CAPÍTULO VII

EFFECTS OF TREATMENTS ON BIOMASS BOTTOM ASH APPLIED TO THE MANUFACTURE OF CEMENT MORTARS

Rosales, J., Cabrera, M., Beltrán, M.G., López, M., & Agrela F.

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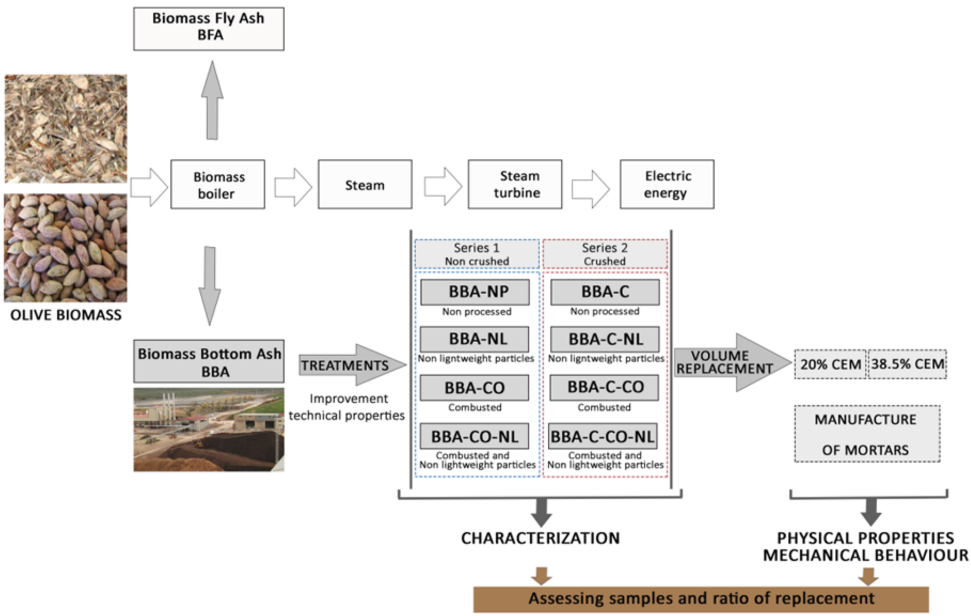
VII

EFFECTS OF TREATMENTS ON BIOMASS BOTTOM ASH APPLIED TO THE MANUFACTURE OF CEMENT MORTARS

Rosales, J., Cabrera, M., Beltrán, M.G., López, M., & Agrela. (2017). Effects of treatments on biomass bottom ash applied to the manufacture of cement mortars. Journal of Cleaner Production, 154, 424-435.



Abstract

The use of biomass for power generation is increasingly common. However, one of the most important problems when using biomass is the amount of waste produced in the combustion process such as ash, which must be transported to landfills for deposition.

Biomass bottom ash may contain a large amount of organic matter which is the most restrictive property for reusing this by-product. The potential reuse is determined by chemical and physical properties. The presence of light particles and organic matter confer to biomass bottom ash certain physical and chemical characteristics which significantly reduce the possibility of reuse. Previous studies have demonstrated the possibility of using biomass bottom ash in cement-treated materials, but its properties imply a decrease of compressive and flexural strength.

Therefore, this paper reported the study of the mechanical and durability properties of mortars containing biomass bottom ash applying different processing methods. Cement was replaced with different rates of substitution of biomass bottom ash and several samples were treated applying different techniques, such as grinding, elimination of lightweight particles and combustion.

The results showed significant improvements in the mechanical and durability properties of mortars in which some treatment were applied. Lightweight particle extraction and organic matter removal by burning considerably improved the mechanical behaviour of the manufactured mortars. Therefore, mortars with crushed biomass bottom ash without floating particles and without organic matter led to a 10% of compressive strength decrease with respect to the control mortar.

Thus, this study displays a possibility of waste valorisation by means of to the reuse of this type of byproduct in mortars and concretes manufacture.

Keywords:

Biomass bottom ash, Treatment, Improving property, Cement mortar, Mechanical behaviour

7.1.- Introduction

Renewable energy is an emerging sector. Currently, natural sources such as the sun and wind are used for power generation. However, the reusing of waste generated by industries in energy production has become more common.

In recent years, the use of biomass to generate heat and electrical energy has increased substantially in the European Community [1]. Biomass produced 14% of the global energy supply [2] which is considered an important source of energy for humans. Biomass has become important in recent years because of the high availability of this by-product. Approximately 220 billion tons per year are estimated to be available [3]. Worldwide studies established that before the 2100 year, the amount of biomass used in global energy production should be between 25% and 46% [4]. Biomass is also considered to be the most promising renewable energy source [5]. According to the European Directive (2009) [6], the production of energy should come from renewable sources in a 20% by the 2020 year. In Andalusia (Spain) there are 17 biomass combustion plants that could provide 22.5% of the total primary energy consumption in the area. The main sources of this potential biomass are olive pruning and other by-products of agriculture from the olive sector [7, 8]

Although the use of biomass is positive for the environment, it also shows some disadvantages, one of the most important is the generation of solid waste [9]. There are two types of wastes, Biomass Bottom Ash (BBA) and Biomass Fly Ash (BFA). BBA are formed by totally or partially burned material and BFA are obtained by the particles extraction that is carried by the gas stream outside of the combustion chamber. In Spain, power production plants using biomass generate 120,000 tons/year of waste [10], of which approximately 64% are BFA and 36% BBA [11]. The amount and quality of ash produced from power plant biomass is strongly influenced by the biomass properties and the combustion technology used by each central [12]. Therefore, the study of the BBA properties is a very important issue in order to determine its use in future applications [13].

Due to the large quantity of these by-products that are accumulated in landfills, several studies have been done to evaluate the potential waste reuse. Its use is conditioned by its physical and chemical properties [11]. According to the physical characteristics of other studied by-product, it was observed that the fineness of the particles and the composition of the waste can provide cementitious properties in cement materials [11]. Because of its similarity to conventional fly ash, BFA has been extensively studied by several authors for its application as a construction material. Cuenca et al. (2013) [14] studied the possible use of this type of fly ash for manufacturing self-compacting concrete. Furthermore, Gomez-Barea et al. (2009) [15] manufactured lightweight boards and brick. Rajamma et al. [16] presented the results of new cement formulations incorporating fly ash from biomass. Subsequently, Cruz-Yusta et al. [17] focused their work on the incorporation of fly ash from burning olive as an alternative raw material in cement mortar formulations.

Currently, there are few studies on the use of BBA in building materials. The use of this by-product is limited in materials with low and medium strength. This by-product is used to partially replace some of the source materials that make up the mix in mortar cement and concrete (cement and aggregate). Due to the low density and high porosity of BBA [18], many studies have used this material as a substitute for the fine fraction of the aggregate in the manufacture of concrete and cement mortar. Studies showed optimum percentage of BBA in mixes to obtain good mechanical strength results [19, 20]. The newly manufactured materials showed a lower weight [19, 21].

Other author's studies such as Demis et al. [22], showed that ashes from agro-industrial by-products have large amounts of silica, which can be an alternative to the addition of cementitious materials that are traditionally used. For this reason, studies by Cabrera et al. [23] demonstrated the cementitious capacity of BBA for its use in cement-treated materials. Beltran et al. [24] evaluated the possibility of replacing natural sand and cement with BBA in bedding mortars. All of the results showed an increase in porosity and a decrease in density in materials made with a percentage of cement replacement by BBA, as well as high organic matter content in these industrial by-products. The organic matter content of BBA is the most restrictive condition/property to use this by-product as an addition in the manufacture of cement treated materials [25]. The organic matter content of BBA affects its durability and mechanical behaviour, as demonstrated by Beltran et al. [24]. This high organic matter content is related to its high water absorption property [26]. For these reasons, it may be advisable to encourage BBA optimization processes, such as removing organic matter with different simple treatments. This organic matter is mostly present in floating particles (which are those with a density of less than 1 g/cm^3) and in unburned particles. The presence of organic matter content in BBA is influenced by the combustion systems of each power production plant. Based on these premises, the main objective of this study was to evaluate the influence of the organic matter content present in BBA to study the mechanical and durability behaviour of cement mortars manufactured with different percentages of BBA as a replacement of cement. To achieve this objective, a simple treatment such as crushing, removal of lightweight particles and combustion was performed; eight different types of BBA materials were obtained.

The physical and chemical properties of unprocessed and processed BBA (crushed, combusted and without lightweight particles) were studied for comparison. The mechanical and durability behaviour of this type of by-product was studied to assess the possibility of using BBA as a hydraulic binder to replace cement. Different percentages of non-processed and processed BBA were applied to the manufacture of cement mortars to determine the optimal replacement rate to increase the economic value of this by-product. By these methods, the influence of the organic matter content for each material on the mechanical behaviour and durability of mortars was determined.

The results showed an improvement in the mechanical and durability behaviour of mortars manufactured with processed BBA (material showing low content of organic matter). For these reasons, it may be advisable to encourage BBA process optimization by performing a basic treatment, such as removing organic matter content to improve the existing biomass combustion process in processing plants.

7.2.- Materials and Methods

7.2.1 - Materials

The present study evaluated olive biomass bottom ash with eight different treatments, not processed (BBA), crushed (BBA-C), combusted (BBA-CO), BBA without lightweight particles (BBA-NL) and treatments combination (BBA-C-CO), (BBA-C-NL), (BBA-CO-NL), (BBA-C-CO-NL). In addition, to evaluate the influence of BBA as a partial replacement for cement, the properties of the cement manufactured with BBAwere compared to those of cement without additions (Control-OPC). Therefore, Control-OPC material was also studied.

Natural sand

A standard natural sand (SNS) was applied as a natural aggregate for the manufacture of mortars. The characteristics of this type of sand are in accordance with the specifications required by the standard DIN 196-1. This type of sand presents a maximum value of 2 mm in grain size distribution (Figure 7.1).

Cement

Ordinary Portland Cement (OPC) type CEM-I 52.5 with rapid hardening and a characteristic strength of 52.5 MPa was used in this work according to ASTM C150. This cement did not contain mineral additions; therefore, the mechanical behaviour of the mortars manufactured with a mixture of cement and BBA is not affected by any type of mineral addition. The chemical composition of OPC was determined by wavelength dispersive X-ray fluorescence (XRF) spectrometry according to UNE EN 196-2 is summarized in Table 7.1. Quantitative X-ray diffraction (QXRD) data were collected using (Panalytical NHM-X226) and quantified using the Super Q software.

The Portland cement is composed for four major oxides: lime (63.75%), silica (20.18%), iron (4.51%) and alumina (4.14%). OPC also contains small amounts of magnesium (0.91%), alkalis (Na_2O and K_2O), and sulphuric anhydride (3.24%).

Table 7.1: *Chemical composition of biomass bottom ash and cement (XRF)*

	Content (%)							
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**K_2O**	**Standard**
OPC	20.18	4.14	4.51	63.75	0.91	3.24	0.75	
BBA	55.35	5.39	2.25	16.57	2.64	0.24	7.67	
BBA-NL	53.78	5.66	2.17	19.78	3.02	0.21	7.19	
BBA-CO	52,12	6.03	2.18	22.99	3.24	0.28	7.54	*UNE-EN 196-2*
BBA-CO-NL	49.77	6.11	2.23	23.68	3.34	0.29	6.78	
BBA-C	41.57	5.68	2.21	22.17	3.16	0.20	6.49	
BBA-C-NL	42.24	6.01	2.35	25.12	3.08	0.29	7.13	
BBA-C-CO	45.29	6.53	2.55	26.15	3.62	0.37	7.07	
BBA-C-CO-NL	46.23	6.01	2.11	27.12	3.11	0.31	6.13	

Biomass Bottom Ash

Biomass Bottom Ash (BBA) from the thermal power plant located in Puente Genil, Córdoba (Spain), was used as an OPC substitute. BBA was obtained from the combustion of several agricultural wastes, such as material pruned from olive trees and other plant materials, called biomass. First, biomass was introduced into a chamber, and then, it was combusted at a temperature of 405°C to generate steam that flows through a closed-loop system. The power plants burn approximately 40% olive cake and 60% wood biomass (poplar, olive and pine). BBA is a by-product generated from the combustion of biomass composed mainly of olive mash. BBA was processed using different methods. Eight types of BBA from the manufacture of lots were studied: Biomass Bottom Ash, as received from the plant, non-processed (BBA); BBA crushed (BBA-C), which was crushed by a grinder and then sieved to obtain a fraction finer than 125 µm; BBA combusted (BBA-CO), which was manufactured with BBA burned up to a temperature of 800°C and maintaining BBA at this temperature for 18 hours; BBA without lightweight particles (BBA-NL), particles were removed by flotation and all combinations among these treatments were also studied (BBA-C-CO), (BBA-C-NL), (BBA-CO-NL), (BBA-C-CO-NL). The physicochemical properties of the materials from the different

BBA treatments according to different Standards are summarized in Table 7.2.

Table 7.2: Physical and chemical properties of Biomass Bottom Ash

Properties		BBA	BBA-NL	BBA-CO	BBA-CO-NL	BBA-C	BBA-C-CO	BBA-C-NL	BBA-C-CO-NL	Standard
Density-SSD (kg/dm^3)		1.86	1.98	1.91	2.03	1.89	1.99	2.09	2.12	*UNE-EN 1097 -6*
Water absorption (%)		21.8	20.7	20.3	19.1	19.6	19.4	18.9	19.4	
Elemental content (%)	*Si*	25.11	27.87	24.96	22.17	24.13	24.22	24.21	25.12	*UNE-EN 196-2*
	Ca	17.17	23.35	16.87	22.96	21.17	19.76	27.08	15.12	
	K	16.87	18.68	14.68	17.12	15.63	15.23	15.98	14.73	
	Mg	2.59	3.04	2.18	2.71	2.61	2.52	2.73	2.29	
	Fe	1.20	2.32	1.09	1.28	1.19	1.12	1.06	1.12	
	Al	1.16	1.27	0.12	1.13	1.09	0.98	1.07	0.99	
	Na	0.21	0.29	0.23	0.27	0.27	0.26	0.26	0.23	
	Ti	0.09	0.1	0.11	0.09	0.07	0.09	0.09	0.08	

As shown in Table 7.2, BBA (1.86 kg/dm^3) showed a low density compared to SNS (2.6 kg/dm^3). BBA had a lower density than traditional natural aggregates [25], due to BBA is composed of particles with a low specific weight [27]). The density of BBA processed increased with respect to BBA untreated, as shown in Table 7.2.

Respect to the water absorption capacity, BBA shown a high value (21.8%). Similar values were obtained by other authors [24, 25]. Density and water absorption are important properties to consider. The presence of high levels of water due to the high absorption can modify the physical parameters of materials made with biomass ash [28, 29]. Water absorption by biomass ash affects to concrete and cement workability [28, 30]. Both properties decreased when a treatment was applied to BBA, as shown in Table 7.2.

The BBA organic matter content (4.34%) is a consequence of the biomass combustion efficiency. BBA is produced from feedstocks with low density and biomass with high moisture and/or ash content (e.g., olive pits) [31, 32]. This factor affects to the mechanical properties of cement mortars [24]. Table 7.2 shows that simple treatments, such as crushing (BBA-C), removal of lightweight particles (BBA-NL) and combustion (BBA-CO), as well as combined BBA treatments produced a significant decrease in the organic matter content, showing a 0.98% organic matter content in materials in which all treatments (BBA-C-CO-NL) were applied.

To evaluate the use of BBA as a replacement for cement in the manufacture of cement mortars, a major chemical analysis of the bottom ash was performed using X-ray fluorescence, as shown in Table 7.1. Biomass Bottom ash contains a mixture typical of olive waste ash, with higher values of silica (55.35%) and limes (17.57%) and high values of potassium (7.67%). BBA treatments showed decrease values of silica and potassium, as well as increased the value of lime, as shown Table 7.1. The presence of chlorine and K_2O in cementitious materials can reduce their durability due to the deterioration of the microstructure [33]. For this reason, the decrease in these values resulting from BBA treatment can be a benefit for its use in cement mortars. However, the increase of lime and silica in BBA treated, as shown in Table 7.1, can lead to increased pozzolanic activity [34]. The sum of the values obtained from silica and lime for BBA was similar to the amount found in common fly ash (59.79%) [35]. BBA treated showed similar silica and lime values to Portland cement (OPC), leading to a cementitious capacity improved. Others studies showed when a portion of the bottom ash is substituted for Portland cement, the Portlandite produced reacts with silica or silicates in the ash in the presence of water to create products similar to those obtained via hydration of cement [36].

Finally, a particle size distribution was generated using sieve granulometry following EN 933-1:2012 for SNS and non-processed BBA and a laser beam from a Malvern Mastersizer 2000 for OPC and processed biomass. The results are shown in Figure 7.1.

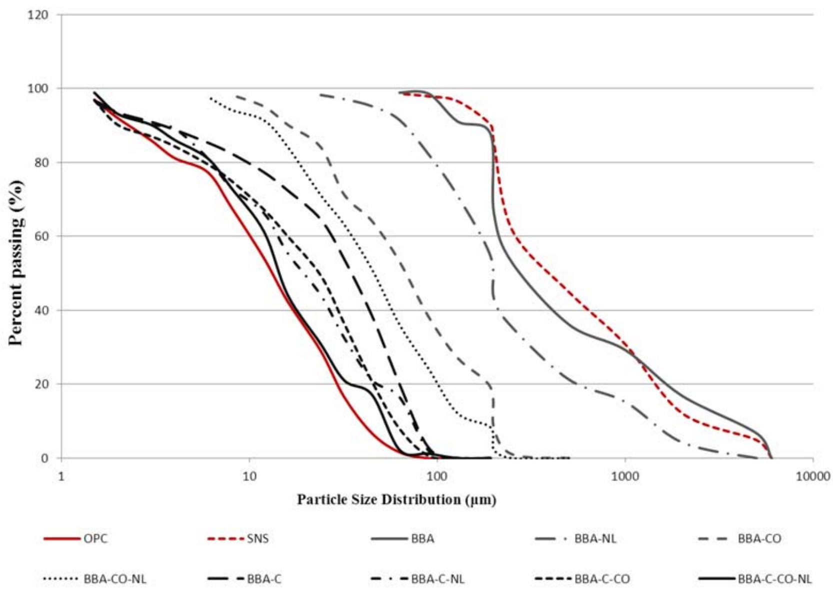


Figure 7.1: Particle size distribution of the different treatments to which has been subjected BBA compared to OPC and SNS

The particle size distribution in biomass bottom ash was continuous. Figure 7.1 shows two different behaviours. In function to the type of material, BBA and BBA-NL showed a particle size distribution similar to that of SNS. However, when the material was crushed, its particle size distribution was similar to that of OPC. This factor can be important for the higher reactivity of bottom ash with cement due to the similar particle size, as noted by Wongkeo et al. [37].

Water-reducing admixture

To obtain similar consistency in all mortars, a plasticizer was used in the manufacture of mortars with BBA at varying contents. The product used, Neoplast, is a high-performance aerating plasticizer with a density of 1040 g/cm^3 and pH = 8. The objective was to reduce the mixing water and allow the cement mortar to be manufactured with a low effective water/cement ratio (w/c) because of its high water reduction.

Mix proportions and manufacture of mortars

Two groups of mortar were manufactured according to the BBA particle size distribution. The first batch of BBA showed a particle size distribution similar to SNS. The second batch was manufactured applying crushed BBA (C), which showed a particle size distribution similar to filler or OPC. Each group consisted in 4 types of mortars according to the system used to process BBA: unprocessed mortar (BBA), mortar with BBA without lightweight particles (NL), combusted mortar (CO) and combusted mortar without lightweight particles (CO-NL). To perform a comparison of results, a control mixture of mortar was added (CONTROL-OPC). In Table 7.3, the nomenclature of mixtures is described.

A mortar sample (Control) with a mix proportion of 0.5:1:3 (water; cement; sand) was designed as the control mix. The by-products (M/BBA, M/BBA-NL, M/BBA-CO, M/BBA-CO-NL, M/BBA-C, M/BBA-C-NL, M/BBA-C-CO, M/BBA-C-CO-NL) were subsequently used as substitute to cement at different replacement levels (20% and 38.5%) for the manufacture of sixteen cement mixes. This replacement was performed in volume, due to the low density of this by-product.

Table 7.3: Nomencalture of cement mortars

MORTAR	DESCRIPTION
CONTROL-OPC	Reference mortar
M/BBA	Mortar with BBA
M/BBA-NL	Mortar with BBA (without lightweight particles)
M/BBA-CO	Mortar with combusted BBA
M/BBA-CO-NL	Mortar with combusted BBA (without lightweight particles)
M/BBA-C	Mortar with crushed BBA
M/BBA-C-NL	Mortar with crushed BBA (without lightweight particles)
M/BBA-C-CO	Mortar with crushed and combusted BBA
M/BBA-C-CO-NL	Mortar with crushed and combusted BBA (without lightweight particles)

The volume of each batch was maintained constant. In Table 7.4 are shown the different quantities of materials applied in the mixtures. Due to the low density of the BBA, the BBA percentage replacement in weight respect to cement was around 13% in the series 1 and 28% in series 2. The mechanical performance and durability properties were tested with six experimental replicates of each sample (Figure 7.2).

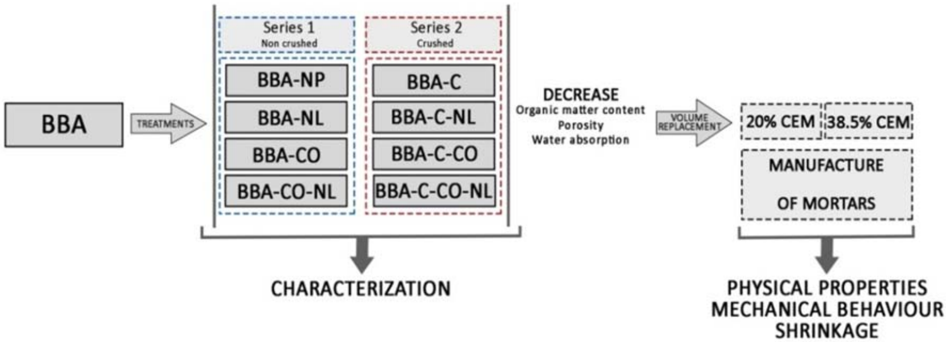


Figure 7.2: Experimental program

The replacement rate of CEM by BBA was 20% by volume in Series 1 and 38.5% by volume in Series 2 for all cases. Moreover, different quantities of additive were added to obtain similar consistency values to the Control-OPC batch, as shown in Table 7.4.

Table 7.4: Mortar mix proportions

		DOSAGE (g)					Total volume (dm^3)
		SNS	BBA	Cement	Water	Additive	
Control	Control – OPC	1350	-	450	225	0	0.66
Series 1 (20% in volume)	M/BBA	1350	53.01	365	225	1.7	0.66
	M/BBA-NL	1350	56.43	365	225	2.1	0.66
	M/BBA-CO	1350	54.44	365	225	2.0	0.66
	M/BBA-CO-NL	1350	57.86	365	225	2.7	0.66
	M/BBA-C	1350	53.87	365	225	1.9	0.66
	M/BBA-C-NL	1350	59.57	365	225	3.1	0.66
	M/BBA-C-CO	1350	56.72	365	225	2.6	0.66
	M/BBA-C-CO-NL	1350	60.42	365	225	3.6	0.66
Series 2 (38.5% in volume)	M/BBA	1350	102.3	280	225	3.1	0.66
	M/BBA-NL	1350	108.9	280	225	4.3	0.66
	M/BBA-CO	1350	105.05	280	225	4.2	0.66
	M/BBA-CO-NL	1350	111.65	280	225	4.6	0.66
	M/BBA-C	1350	103.95	280	225	4.0	0.66
	M/BBA-C-NL	1350	114.95	280	225	5.6	0.66
	M/BBA-C-CO	1350	109.45	280	225	5.3	0.66
	M/BBA-C-CO-NL	1350	116.6	280	225	5.9	0.66

Manufacturing of the mortars was conducted following the guidelines set by the UNE-EN 196-1. Materials were introduced into a mixer with low rotation speed (280 rpm). First, mixing and saturation water and a superplasticizer were gradually added to the mixer, followed by the cement. Second, SNS and BBA were added. The mixing process lasted 3 minutes.

The slump was measured for all batches using a shaking table, as described in the UNE-EN 1015-3. Then, the moulds were filled and vibrated into two layers using a vibrating table to homogenize the fresh mortar specimens. Finally, the moulds were placed in a curing chamber with a humidity of 50% and a temperature of 20°C for 24 hours. After 24 hours, the moulds were immersed in a water tank.

7.2.2 - Experimental methods

This study was conducted to ascertain the mechanical behaviour and durability properties of cement mortars manufactured with non-processed and processed biomass bottom ash. For this reason, series with different degrees of substitution of cement by BBA for the manufacture of cement mortar were studied. Through analysing different properties of the manufactured mortars, the cementitious properties of the BBA and the influence of the treatments was evaluated. To check the influence of by-product processing on the mechanical and durability behaviour of mortars and to determine the optimal replacement ratio to increase the economic value of this by-product, different BBA percentages processed as described above at levels of 20% and 38.5% by volume were applied. Thus, it is possible to observe how the properties of the cement manufactured with BBA differed with respect to cement without additions (Control-OPC).

The hardened mortars were characterised according to seven properties: consistency, dry bulk density, porosity, water absorption, compressive and flexural strength and dimensional instability (shrinkage). Six pieces of each specimen were evaluated.

Consistency

The consistency of the fresh mortar was determined after the manufacture of each mortar. To measure the consistency, a shaking table was used according to UNE-EN 1015-3. Consistency was kept constant to compare the mortars under equivalent circumstances by changing the superplasticiser content.

Density, porosity and water absorption

The dry bulk density and water absorption due to capillarity were determined at 28 days of age by applying prismatic specimens of dimensions of 40 x 40 x 160 mm according to UNE-EN 1015-10.

Porosity was measured using the following procedure: the weight immediately after curing and the weight after 24 h in an oven at 105°C were measured. Porosity is the ratio between the loss of weight and the initial weight; the result is expressed as a percentage. To check the internal porosity qualitatively, samples were analysed using Scanning Electron Microscopy (SEM) at 28 days. The signals generated during the analysis produced a two-dimensional image and revealed information about the sample, including its external morphology (texture).

Compressive and flexural strength

The compressive and flexural strength were measured at 1, 7, 28 and 90 days according to UNE-EN 196-1. A hydraulic press was used to apply a load at a constant speed.

Shrinkage

To determine the dimensional stability, the specimens were first cured at a room with 20 ± 1ºC and 95 ± 5% relative humidity for 3 days. Then the specimens were installed on the measuring device for drying shrinkage at a room with 20 ± 1ºC and 65 ± 5% relative humidity. Finally, shrinkage was measured at 1, 7, 14, 28, 56 and 90 days according to UNE 83831.

7.3.- Results and discussion

Once the experimental program developed in the present work has been defined, the results obtained are shown below.

Consistency

Similar consistency values to the control mortar mixture were obtained from all BBA mortars because a super-plasticizer additive was added. To achieve this consistency, preliminary tests were conducted using several amounts of additive in each mortar. Table 7.5 shows the results of this test.

Table 7.5: Density, porosity and water absorption of hardened mortars

			Consistency (mm)	**Dry bulk density (kg / dm^3)**	**Porosity (%)**	**Water absorption (kg / (m^2·min$^{1/2}$))**
		Day	0	28	28	28
Control		Control – OPC	220	2.32	9.12	3.4
Series 1 (20% replacement of cement)	Non-Crushed (non C)	M/BBA	221	2.14	10.86	5.12
		M/BBA-NL	218	2.15	10.83	5.09
		M/BBA-CO	219	2.17	10.81	5.08
		M/BBA-CO-NL	218	2.18	10.79	5.06
	Crushed (C)	M/BBA-C	220	2.15	10.62	5.04
		M/BBA-C-NL	219	2.15	10.58	5.00
		M/BBA-C-CO	219	2.18	10.57	4.98
		M/BBA-C-CO-NL	221	2.19	10.55	4.97
Series 2 (38.5% replacement of cement	Non-Crushed (non C)	M/BBA	218	2.07	11.54	6.4
		M/BBA-NL	219	2.09	11.42	6.3
		M/BBA-CO	220	2.11	11.41	6.1
		M/BBA-CO-NL	221	2.10	11.38	6
	Crushed (C)	M/BBA-C	221	2.08	11.31	5.9
		M/BBA-C-NL	218	2.09	11.29	5.6
		M/BBA-C-CO	219	2.11	11.28	5.5
		M/BBA-C-CO-NL	221	2.12	11.19	5.3

Density, porosity and water absorption of hardened mortars

The physical properties, including density, porosity and absorption parameters, were studied for hardened mortars to 28 days.

Previous works demonstrated that the density of materials-based cement is mainly dependent on the density of the aggregates used [38]. Therefore, the data for the dry bulk density (Table 7.5) decreased slightly as more biomass bottom ash is substituted for Portland cement due to the lower density of BBA compared to OPC. For this reason, the change in this property is conditioned to the physicochemical characteristics of BBA (Table 7.2). Similar density values were obtained comparing the two sets of mortars (with crushed and non-crushed material), (Table 7.5). Therefore, the density of mortars was not increased with crushed BBA. Nevertheless, the density was increased extracting lightweight particles and eliminating organic matter from both series, as expected. However, density increased was not significant.

The decrease in apparent density, in turn, led to an increase in the porosity of the samples, thus, the water penetration increased due to the hydration products and pozzolanic materials that filled the voids in the cement paste [39]. As expected, the use of highly porous industrial by-products, such as BBA, increased the porosity significantly in hardened cement mortar. However, the porosity was lower in mortar with crushed BBA with respect to mortar with non-crushed BBA. Analysing the effects that the processed BBA caused, Table 7.5 shows that BBA processed (without lightweight particles and combusted) decreased in relation to the porosity to unprocessed BBA) in each series. In the two sets of mortars (with material crushed and non-crushed) the lowest porosity values were obtained when BBA was crushed, combusted and lightweight particles were removed (M/BBA-C-CO-NL).

However, as shown in Table 7.5, the values for water absorption in the samples after curing for 28 days increased slightly as more biomass bottom ash was substituted for Portland cement, indicating that there were open pores in the structure (like porosity values). The use of crushed BBA reduced the water penetration values.

Therefore, the results obtained showed that water absorption is directly related (R^2 = 0.9179) to the amount of voids, so the absorption decreased as the amount of voids decreased, as shown in Figure 7.3. The highest correlation values were obtained for Series 1, in which the replacement ratio was 20%.

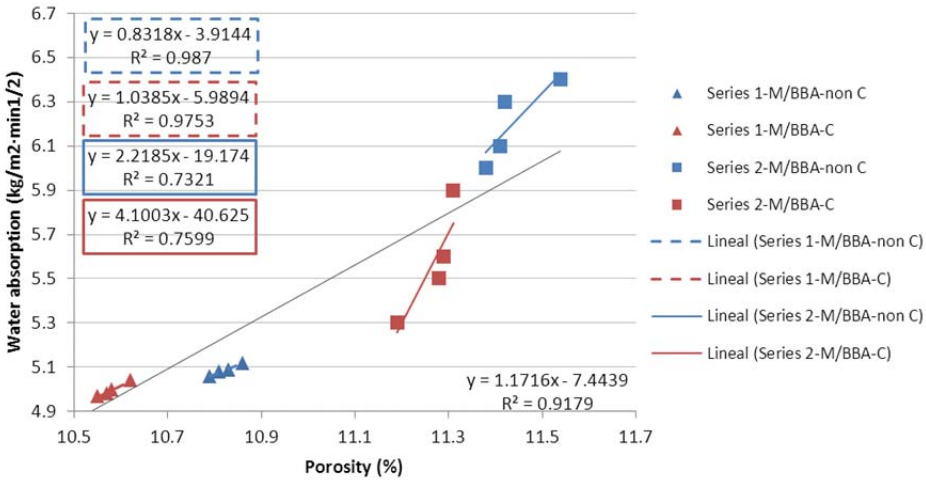


Figure 7.3: Correlation between porosity and water absorption

Based on the above-mentioned results, we can observe that water absorption is an extremely important property for mortars. In fact, high values of water content in cement mortars could become damages and cause efflorescence phenomena due to expose to environmental condition [40].

For this reason, an analysis via Scanning Electron Microscopy (SEM) at 28 days was performed. The porous structure (Figure 7.4) of the SEM microscopy confirmed the structural cohesion, as well as the distribution. A high porosity surface was observed in the samples with the highest percentage of BBA. Similar values were observed in previous studies [13, 24].

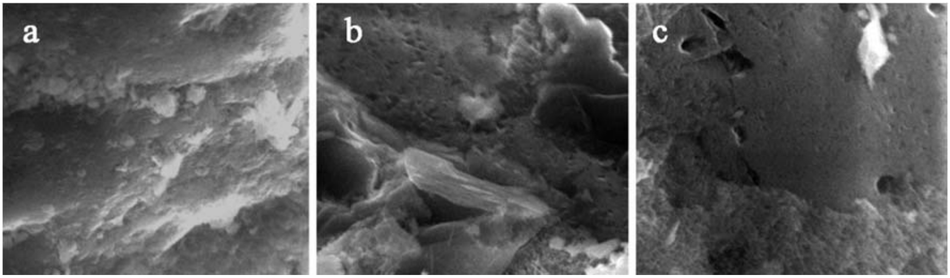


Figure 7.4: Micromorphology of cement mortars. (a): Control mortar-OPC; (b): Mortar with 20% of BBA; (b): Mortar with 38.5% of BBA

Compressive and flexural strength of hardened mortar

Table 7.6 shows the results for the compressive and flexural strengths of the different series of mortars. As expected, the compressive strength increases progressively with time [41, 42]. An increase is observed according to the curing age (Table 7.6).

Table 7.6: *Compressive and flexural strength of hardened mortar*

			Age (Days)					Age (Days)			
			1	**7**	**28**	**90**		**1**	**7**	**28**	**90**
Control - OPC		**Compressive strength (MPa)**	20.31	48.29	58.03	62.09	**Flexural strength (MPa)**	5.97	8.03	10.33	11.96
Series 1 (20% replacement of cement)											
Non-Crushed (non C)	**M/BBA**	**Compressive strength (MPa)**	10.08	19.54	25.12	28.46	**Flexural strength (MPa)**	2.98	5.62	7.28	9.03
	M/BBA-NL		12.16	22.15	27.61	32.05		3.05	6.07	7.71	9.28
	M/BBA-CO		13.03	24.27	29.12	35.21		3.11	6.11	8.05	9.32
	M/BBA-CO-NL		15.58	27.06	33.21	38.87		3.24	6.24	8.24	9.56
Crushed (C)	**M/BBA-C**		11.01	29.56	36.18	41.87		3.05	5.97	8.01	9.73
	M/BBA-C-NL		14.18	33.54	38.92	44.15		3.54	6.29	7.96	9.98
	M/BBA-C-CO		15.04	36.82	44.17	48.91		3.22	6.19	8.04	10.2
	M/BBA-C-CO-NL		19.18	44.12	51.96	54.34		4.11	7.04	9.25	11.24
Series 2 (38.5% replacement of cement)											
Non-Crushed (non C)	**M/BBA**	**Compressive strength (MPa)**	5.26	17.51	20.63	23.47	**Flexural strength (MPa)**	1.93	4.22	6.45	7.48
	M/BBA-NL		7.78	19.36	23.88	29.31		2.74	4.63	6.59	7.68
	M/BBA-CO		8.43	24.12	27.66	32.28		2.87	5.14	6.74	8.35
	M/BBA-CO-NL		15.54	25.49	30.47	34.36		3.95	5.72	7.38	8.54
Crushed (C)	**M/BBA-C**		9.27	23.12	32.61	35.86		2.93	5.38	7.14	8.62
	M/BBA-C-NL		11.94	29.18	36.97	40.33		3.01	5.72	7.48	8.85
	M/BBA-C-CO		12.23	32.16	40.15	42.97		2.73	5.34	7.89	9.61
	M/BBA-C-CO-NL		17.06	39.42	47.28	49.64		3.63	5.81	8.87	11.15

The results showed that all mortars with incorporated BBA showed a lower compressive strength with respect to Control-OPC. These values were obtained previously by other authors. Carrasco et al. [13] showed in their work how the compressive strength decreased in building blocks incorporating BBA. Similar values were obtained by Beltran et al. [24]. Rajamma et al. [26] demonstrated that the differences between samples cured for up to 28 days were minor, but the absolute values were lower in all mortars with the addition of BFA with respect to a control mixture.

The compressive strength decreased with respect to the control OPC in Series 1 and 2 according to an increase in BBA amount for all aging periods and all samples (Table 7.6 and Figure 7.5). Lower compressive strength losses occurred in cement mortars with non-processed BBA (M/BBA). The strength loss was 65% compared to Control-OPC. However, these values were substantially reduced when biomass bottom ash was crushed (Figure 7.5). For mortars with crushed BBA in Series 2, the loss of compressive strength was 44-36% for M/BBA-C and M/BBA-NL-C and 31-18% for M/BBA-C-CO and M/BBA-C-CO-NL. Nevertheless, in cement mortar with a 20% replacement ratio, this loss of compressive strength was reduced. Cement mortars that were crushed had the organic matter content removed showed a 10% of loss of compressive strength with respect to the control mixture.

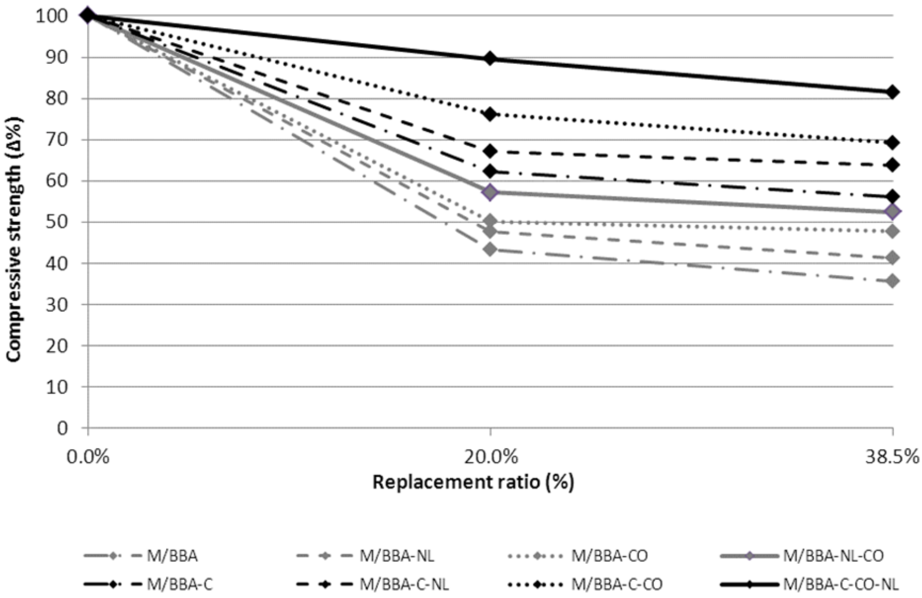


Figure 7.5: Variation of the compressive strength versus replacement ratio

These results indicate that the extraction of light particles and removal of organic matter from combustion significantly improves the compressive strength.

However, high values of SiO_2 and CaOH produce pozzolanic reactions. These values increase when BBA is processed, resulting in a positive cementitious capacity in the by-product [34], as shown Figure 7.6. Comparing the results obtained from silica and lime in Table 7.1, the chemical composition of biomass bottom ash and cement (XRF) were analysed, and the results of compressive strength obtained show a high correlation. This ratio was higher in mortars with a higher content of BBA, demonstrating the relationship that the composition of these by-products showed with compressive strength.

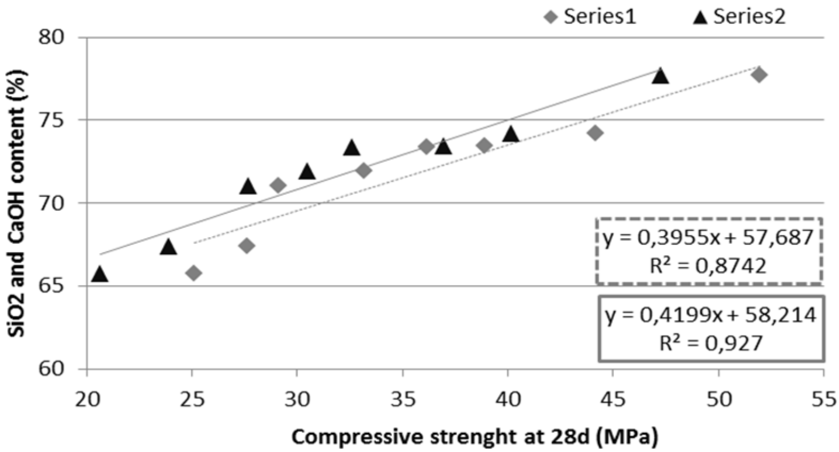


Figure 7.6: Correlation between compressive strength at 28 days and SiO_2 and CaOH content

Similar values were obtained for flexural strength. The compressive strength can reliably determine the flexural strength for each mortar, and vice versa. These results are corroborated by previous studies [24,26] in which the flexural strength of manufactured mortars with different wastes as a substitute for cement decreased with the increase in the percentage of substitution

Moreover, other factors, such as the high organic matter content present in BBA (4.34%), may cause a reduction in the compressive strength relative to high water absorption [26] and its high susceptibility to abrasion.

Analysing these factors, a high correlation between the compression strength and water penetration values is observed in all samples (Figure 7.7). As the degree of substitution increases, the correlation between both properties increases (R^2 = 0.9843) because the increased presence of BBA in cement mortars causes a larger amount of organic matter, a higher rate of production of pores and increased water absorption, leading to a substantial reduction in compressive strength.

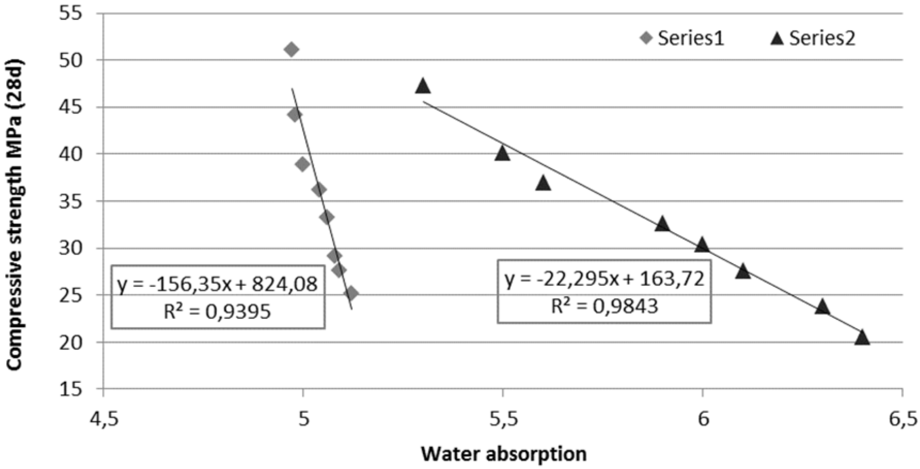


Figure 7.7: Correlation between compressive strength and water absorption at 28 days

Shrinkage

To evaluate the use of BBA as a replacement for cement in cement mortars, it is necessary to study the dimensional instability produced in the cement mortar mixtures. A study of shrinkage was performed over a long time. The results show a trend similar to linear shrinkage (µm/m) over time (Figure 7.8).

Shrinkage was higher for all mortars with an addition of BBA relative to the Control for all ages and measurements.

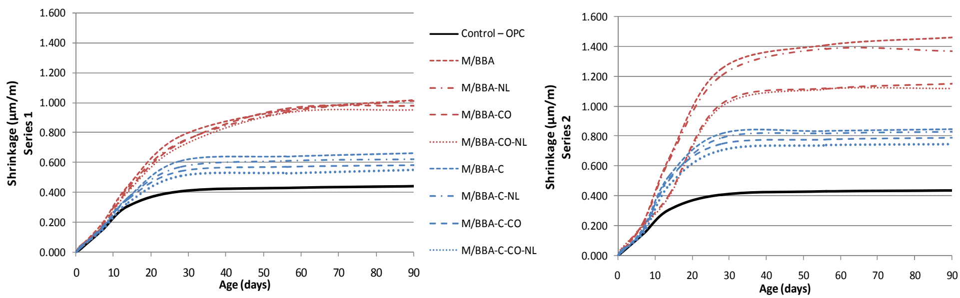


Figure 7.8: Shrinkage of the mortar as a function of age in days

Figure 7.8 shows that mortars made with a degree of substitution of BBA have values above the mortar shrinkage control. However, this figure shows that the total drying shrinkage of the cement mortars with 20% BBA in 90 days showed values near the Control-OPC.

BBA that were processed by calcination had controlled shrinkage values, reducing shrinkage if BBA was combusted and light particles were removed.

These results are similar to those of other studies conducted on the use of biomass ash as a substitute for cement or aggregates in cement mortars [43], where shrinkage was higher relative to the Control OPC cement in mixes with BBA, indicating that the use of ash as a replacement tends to induce stronger dimensional changes.

The dimensional changes are mostly due to the porosity of the material [44], according to the degree of substitution in the manufacture of cement mortars. As the substitution percentage increases, a higher correlation between porosity and shrinkage is observed, as shown in Figure 7.9. For this reason, the values are strongly dependent on the development of the microstructure upon curing [45].

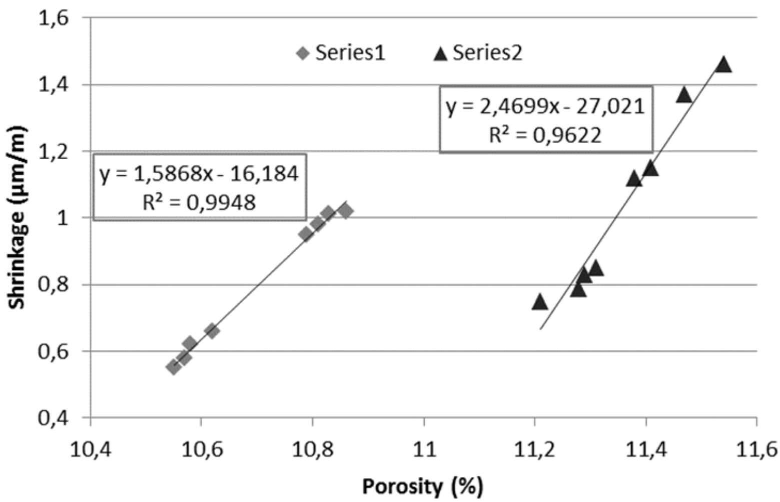


Figure 7.9: Correlation between shrinkage at 90 days and porosity at 28 days

7.4.- Conclusions

This work evaluates the use of olive biomass bottom ash as a cement substitute in cement mortars manufacturing as well as the influence of organic matter content in mortars made with BBA. In order to improve the mechanical behaviour of mortars it has been used different processes to reduce the organic matter content.

The following specific conclusions were obtained:

- Unprocessed BBA showed high values of water absorption, high organic matter content and low density. The values of water absorption and organic matter content decreased when BBA was crushed. A suitable particle size distributionwas obtained when the material was crushed, similar to Cement-OPC.
- BBA contained significant levels of alkaline salts (K_2O and MgO) which caused a worsening of the durability behaviour of mortars. Processed BBA showed lower values of these components.
- High values of SiO_2, Al_2O_3 and CaOH were obtained in processed BBA. These values provided pozzolanic reactions and positive cementitious capacity.
- The BBA addition caused a worsening in the mechanical behaviour. However, minor reductions in compressive and flexural strength were obtained for mortars in which previous treatments BBA were conducted. The highest values of compressive strength were obtained in mixtures with M/BBA-C-CO-NL compared to Control, applying a 20% substitution of cement.
- Similar shrinkage values were obtained in mixtures with 20% processed BBA replacement compared with Control-OPC. The low organic matter values and low porosity values obtained in processed BBA lead to a better behaviour against external agents, which results in a shrinkage values reduction.

Finally, the following general conclusions were obtained:

- The use of BBA in the manufacture of cement mortars produces a significant reduction in the compressive strength. The application of processed BBA significantly improves the mortars properties, which allows its use in the cement mortars manufacture.

- Applying combustion and crushing processes, an increase of 80% in the compressive strength of the mortars are achieved for 20% of substitution respect to unprocessed BBA mortars and an increase of 100% in this property with substitution of 38.5% were observed.
- Therefore, it is demonstrated that the application of processed BBA as a substitute to cement in the production of mortars is feasible by crushing and combustion treatments. Additionally, a light particle removal treatment can be applied but it is expensive and difficult process.

7.5.- Standards used in the experimental work

- ASTM C150. Standard Specification for Portland Cement.
- UNE-EN 196-2:2014. Method of testing cement - Part 2: Chemical analysis of cement.
- UNE-EN 1097-6:2014. Tests for mechanical and physical properties of aggregates - Part 6: Determination of particle density and water absorption.
- UNE-EN 1744-1:2010. Tests for chemical properties of aggregates - Part 1: Chemical analysis.
- UNE 103204:1993. Organic matter content of a soil by the potassium permanganate method.
- UNE-EN 933-1:2012. Tests for geometrical properties of aggregates - Part 1: Determination of particle size distribution - Sieving
- method.
- UNE-EN 196-1:2005. Methods of testing cement - Part 1: Determination of strength.
- UNE-EN 1015-3:2000. Methods of test for mortar for masonry. Part 3: Determination of consistence of fresh mortar (by flowtable).
- UNE-EN 1015-10:2000. Methods of test for mortar for masonry -Part 10:

Determination of dry bulk density of hardened mortar.

- UNE 83831:2010 EX. Methods of test for hardened mortar for masonry - Determination of dimensional stability of hardened mortar for masonry.

7.6.- Acknowledgements

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CAPÍTULO VIII

EFFECTS OF STAINLESS STEELS SLAG WASTE AS A REPLACEMENT FOR CEMENT IN MORTARS. MECHANICAL AND STATISTICAL STUDY

Rosales, J., Cabrera, M., & Agrela, F.

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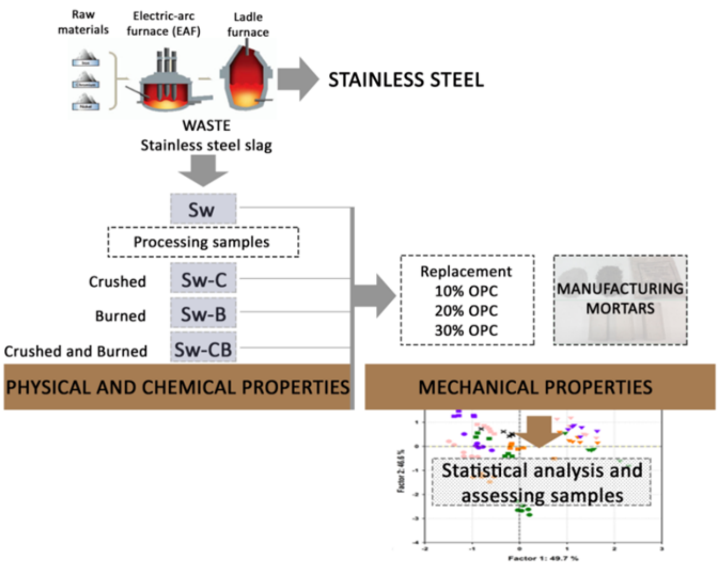
VIII EFFECTS OF STAINLESS STEELS SLAG WASTE AS A REPLACEMENT FOR CEMENT IN MORTARS. MECHANICAL AND STATISTICAL STUDY.

Rosales J., Cabrera, M., Agrela, F. (2017). Effects of Stainless Steel Slag Waste as a replacement for cement in mortars. Mechanical and statistical study. Construction and Building Materials, 142, 444-458.



Abstract

This document studies replacing cement by stainless steel slag waste and improving the mechanical properties of the slag waste by using different types of treatments.

The application of stainless steel slag waste reduces the use of raw materials for manufacturing cement and provides a profit from the large amount of waste generated.

This study analyses the cementation and pozzolanic reaction characteristics of stainless steel slag waste to evaluate its strength activity index and its environmental impact. The cement was replaced with different substitution percentages of untreated stainless steel slag waste and slag waste that was processed through crushing, burning and both treatment to determine the optimum replacement ratio according to its mechanical properties. A study based on multivariate factor analysis was developed to compare these processed wastes according to their mechanical behaviour. The decision mechanism consists of a feature extraction method to evaluate the wastes used as a cement substitute.

Keywords:

Stainless steel slag waste, Cement substitute, Mechanical behavior, Statistical study

8.1.- Introduction

Stainless steel production is currently one of the most dynamic sectors of the manufacturing industry due to a large increase of the use of this product in the construction and industrial sectors; considerable amounts of waste are generated from these factories [1,2]. These high amount of waste generated is not only a quantity crisis but also an environmental problem [3–6]. For every three tons of stainless steel produced, approximately one ton of slag waste is generated [1].

Steel slag is a by-product of the steelmaking and steel refining processes. Different types of steel slag are generated from basic oxygen-furnace (BOF) steelmaking, electric-arc-furnace (EAF) steelmaking and ladle-furnace steel refining processes [7]. In the first process stage (BOF or EAF), steel slag is a by-product of the aggregate [8,9]. However, in the second stage of manufacturing stainless steel (ladle-furnace steel refining), stainless steel slag is generated as dust. The dusts are the most important by-product of stainless steelmaking and refining operations. It is understood as dust, the particles with mean diameter of 3 µm. Approximately 1–2% (mass fraction) of raw materials charged in the smelting furnaces enters into the exhaust gases and is then converted into dust [10]. This slag dust requires more storage space and has less market value than the aggregate slag used in the construction sector [11].

Currently, both slags are generally treated as waste and dumped in landfills. Alternative uses for these stainless steel slags could be applied. There are several previous studies for the application of steel slags [12]. Stainless slag can be used as landfill liner materials or for cement adhesives and roadbed materials after undergoing a stabilization/solidification process or other methods [12,4]. In practice, compared with blast furnace slag, the application scope of steelmaking slag is limited to the production of aggregates for road pavement or concrete [13–15].

Previous papers have studied the cementitious properties of steel slag [16]. According to these studies, this type of waste could be used in the manufacture of cement. The cement industry is researching possible revisions in the manufacturing process and in the selection of raw materials [17]. Currently, 0.97 tons of CO_2 are produced for each ton of clinker [18]. The goal of the cement industry is to reduce CO_2 emissions by 50% in 2050 [17]. One of the primary paths toward reaching this goal is reducing the clinker content in cement. The use of stainless steel slag waste as a supplementary cementitious material can be of great interest in this context [16].

The amount of waste produced from the stainless steel industry must be considered as along with the toxic waste, such as nickel, lead, chromium or cadmium, generated by landfill storage of this waste [2,9]. These toxic elements can cause environmental damage. The presence of minor constituents in any substance or product, whether natural or artificial, plays an important role in their properties. It is necessary to detect the nature and concentration of these elements. Among the minor constituents of Portland cement that deserves special attention is chromium, which affects both cement properties (varying the short-term and long-term mechanical strength, changing the colour of white cements, controlling the corrosion of concrete reinforcement etc.) and its toxic-polluting consequences [19].

It must be considered the amount of waste produced from stainless steel industry, as well as waste generated by storage in dump, such as nickel, lead, chromium or cadmium [2,9]. These elements can present environmental damages. This study through the analysis of the leaching of heavy metals proves that the material shows high values of Cr but this metal is presented as Cr (III). The presence of chromium in cements (20–160 ppm) is due mainly to the raw materials used in cement manufacture [20] that contain chromium as an impurity. The use of stainless steel slag waste (Sw) in cement manufacturing involves analysing the presence of chromium VI because there this toxic element is limited according to the current Spanish legislation for the manufacture of cement. Chromium content was evaluated according to UNE-EN 196-10, and it was shown that it is not detrimental to the environment or human health. The values of Cr (VI) decreased when the waste is presented inside the cementitious matrix, and this material did not exceed the levels required by the standards for cement. Previous works corroborate this reduction of Cr VI [2]. These studies demonstrated through different treatments that the presence of heavy metals in stainless steel slag waste could be reduced. In addition, to evaluate the environmental impact of the presence of Cr VI in the cement matrix manufactured with Sw, this study aims to calculate the cementitious properties of Sw. Other studies previously demonstrated that these wastes exhibit cementitious properties under the influence of chemical activators [21]. According to its microstructural morphology, chemical composition and X-ray diffraction spectrum, Sw is typically composed mainly of calcium oxide, silica, magnesium and aluminium oxides. The potential value and the fineness of the waste suggest that these wastes can be used as a supplementary cementitious material [22,23]. According to the physical characteristics of other residues studied, it was observed that the fineness of the particles and the composition of the waste can provide cementitious properties in cement materials [24].

Recent studies have discussed the application of stainless steel slag in cement material but with only 10% cement replacement [25]. It is also possible to use Sw as part of the sand and cement in mortar manufacturing for the construction industry, replacing up to 30% of cement [26]. To increase the final concrete strength, researchers have suggested several ways of processing the raw material such as re-melting [23], use of activators [27] or crushing and screening [28,29]. It should be noted that the presence of free lime and magnesia could cause problems in restrained structural members due to delayed expansion phenomena [30].

Crushing and burning Sw can improve the reactivity and strength of the cementitious components [31,32]. Previous studies showed that some slag has better properties for use as a cement additive when subjected to simple processes, suggesting Sw processing to obtain a higher strength in manufactured cement. In this study, the possibility of using Sw as a partial replacement of cement was analysed; this material was processed through crushing, burning and both.

In the present study, the physical and chemical properties of unprocessed stainless steel slag waste, crushed slag waste and burned slag waste were studied for comparison. The environmental effects applying leaching test and mechanical behaviour of this type of waste were studied to assess the possibility of using stainless steel slag as hydraulic binders to replace cement. Different percentages of non-processed (Sw-N), crushed (Sw-C), burned (Sw-B) and crushed and burned (Sw-CB) Sw were applied in the manufacture of cement mortars to determine the optimal replacement rate to increase the economic value of this waste and to determine the influence of waste processing in the mechanical behaviour of mortars. To evaluate the use of stainless steel slag waste in cement mortars and to classify it according to its durability, mechanical behaviour and its environmental impact, a multivariate analysis was applied to the cement mortars studied.

8.2.- Materials

The present study evaluated four stainless steel slag wastes processed including unprocessed (Sw-N), crushed (Sw-C), burned (Sw-B), and a combination of both crushed and burned (Sw-CB) Sw. In addition, to evaluate the influence of Sw as a partial replacement of cement, the properties of the cement manufactured with Sw were compared to cement without additions (Control-OPC) and with a common addition (Control-FA). Therefore, both materials were also studied.

Figure 8.1: Materials used in the manufacture of cement mortar. OPC-CEM I 52,5R(a), Natural sand (b), Common Fly Ash (c), Stainless steel slag unprocessed (d), Stainless steel slag crushed (e), Stainless steel slag burned (f) and Stainless steel slag crushed and burned (g).

Cement – ordinary Portland cement (OPC)

In this work, CEM I 52,5R was used; this cement does not contain mineral additions. Therefore, the behaviour of the mortar with the addition of stainless steel slag waste is not conditioned by the components present in the cement. The water used was potable water, and CEN Standard Sand (NS) was used; these materials are shown in Figure 8.1. The chemical properties of the cement are shown in Table 8.1.

Table 8.1: Properties of OPC.

CEMENT	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Loss on ignition (975°C)
OPC	19.58	4.41	2.5	64.18	0.94	3.37	0.93	2.58

Common fly ash (FA)

Fly ash is the most widely used pozzolanic material due the improvements in workability caused by the sphericity of these particles and its particle size distribution [33, 34]. Moreover, fly ash can also improve the mechanical strength and durability of concretes over long-term curing times. Therefore, common fly ash (Figure 8.1) was studied to compare and evaluate its physical (Table 8.2) and chemical (Table 8.3) properties with Sw; the mechanical properties acquired by these cements with different replacements were also compared.

Stainless steel slag waste (Sw)

Four types of Sw produced by the steel plant Acerinox in Algeciras, Cádiz, were studied: Sw-N, Sw-C, Sw-B, Sw-CB. The steel slag was produced during the direct reduction of iron in an electric arc furnace. For the manufacture of lots, Sw was processed using different methods. Four materials were obtained: unprocessed stainless steel slag waste (Sw-N), crushed stainless steel slag waste (Sw-C) that was crushed by a grinder and then sieved with a fraction finer than 125 lm, burned stainless steel slag waste (Sw-B) that was manufactured with stainless steel slag waste that was burned at a temperature of 800°C for 18 h and crushed and burned stainless steel slag waste (Sw-CB) that was manufactured with slag that underwent both crushing and burning process. Figure 8.1 shows the different types of unprocessed and processed Sw.

The physicochemical properties of the different Sw according to different standards are summarized in Table 8.2. Particle size distribution, uniformity factor and specific surface area (SSA) are important physical parameters affecting cement service properties. These parameters define the proportion of fine and coarse particles in the cement. This proportion controls water demand, setting and hydration reactions [35]. For this reason, regarding the physical properties of the materials, the particle size distributions of the OPC, FA and Sw were also analysed. This property was determined using low angle laser light scattering LALLS (Malvern Mastersizer). Size fractions play different roles in strength development during early and late ages. Other properties influenced by particle size distribution are heat release, capillary porosity percolation, diffusivity, shrinkage and microstructure [36].

Table 8.2: Physical and chemical properties

PROPERTIES		FA	Sw-N	Sw-C	Sw-B	Sw-CB	test method
Density-SSD (kg/m3)	0-4 mm	1.23	2.10	1.84	1.64	1.61	**UNE - EN 1097 - 6**
Water absorption (%)	0-4 mm	4.97	5.84	4.65	4.89	4.73	
Elemental content (%)	**Si**	53.21	22.49	20.70	19.84	19.91	**UNE 196-2:2014**
	Ca	0.98	27.26	27.98	25.89	26.15	
	K	1.23	0.75	0.02	0.03	0.02	
	Mg	0.98	6.07	6.30	5.55	5.73	
	Fe	6.12	0.63	1.13	0.79	0.94	
	Al	17.31	2.06	1.96	1.74	1.83	
	Na	0.06	0.26	0.04	0.06	0.06	
	Ti	0.21	0.85	0.98	0.83	0.87	
Sulphate (%SO_4)		0.13	0.1	0.1	0.38	0.23	**UNE - EN 1744-1**

Figure 8.2 shows a continuous distribution for all materials. The OPC and FA cement showed similar particle size distributions. These materials showed smaller particles than Sw. Comparing Sw-N with different treatments, the Sw-C material had a finer distribution of the remaining material particles. This was expected because the processing of this material involved crushing and sieving.

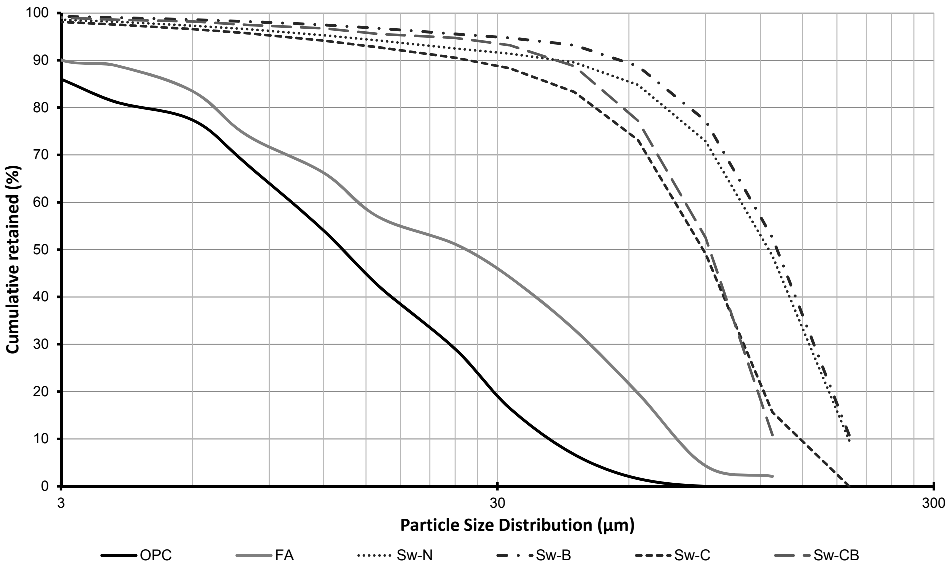


Figure 8.2: Particle size distribution of the different treatments to which has been subjected Sw compared to OPC and FA. Test conducted using laser diffraction Malvern Mastersizer

The chemical analysis of the slag was determined using energy dispersive X-ray fluorescence spectrometry (EDXRF) according to UNE EN 196-2. Quantitative X-ray fluorescence (QXRF) data were collected using Panalytical NHM-X226 and quantified using the Super Q software; the samples were fused and analysed by the Rietveld method. Table 8.3 shows the oxide composition of the FA and Sw determined using QXRF analysis.

Table 8.3: Physical and chemical properties

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Loss on ignition (975ºC)	test method
FA	56.09	26.61	7.26	1.37	1.35	0.15	2.54	1.04	**UNE-EN 196-2**
Sw-N	30.43	6.00	0.94	46.21	9.98	0.39	0.00	0.75	
Sw-C	29.55	5.67	1.3	45.62	10.41	0.37	0.00	1.11	
Sw-B	30.74	5.61	1.96	45.37	10.61	0.33	0.00	0.05	
Sw-CB	30.21	5.78	1.31	46.82	10.77	0.38	0.00	0.02	

The Sw presented only a minor content of Fe oxide, as shown in Figure 8.3. The composition of a common fly ash was shown as a reference. The values obtained with respect to the composition of oxide materials were similar for the four samples studied.

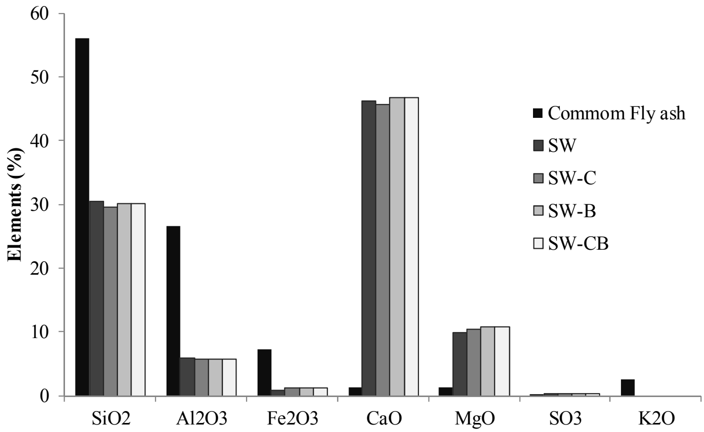


Figure 8.3: Main oxides in the investigated stainless steel slag waste compared to Common fly ash.

Through the Quantitative X-ray fluorescence analysis (QXRF), the different types of slags processed were analysed to compare their predominant elements with a common fly ash, as shown in Figure 8.4.

Figure 8.4 shows that Sw presented a high Ca content and that FA showed a high Si content; however, the other major chemical components were similar in both materials. Similar results were obtained in earlier studies [32] which showed that stainless steel slag is mostly composed of gangue materials, such as CaO, SiO_2, Al_2O_3, MgO and some metal oxides.

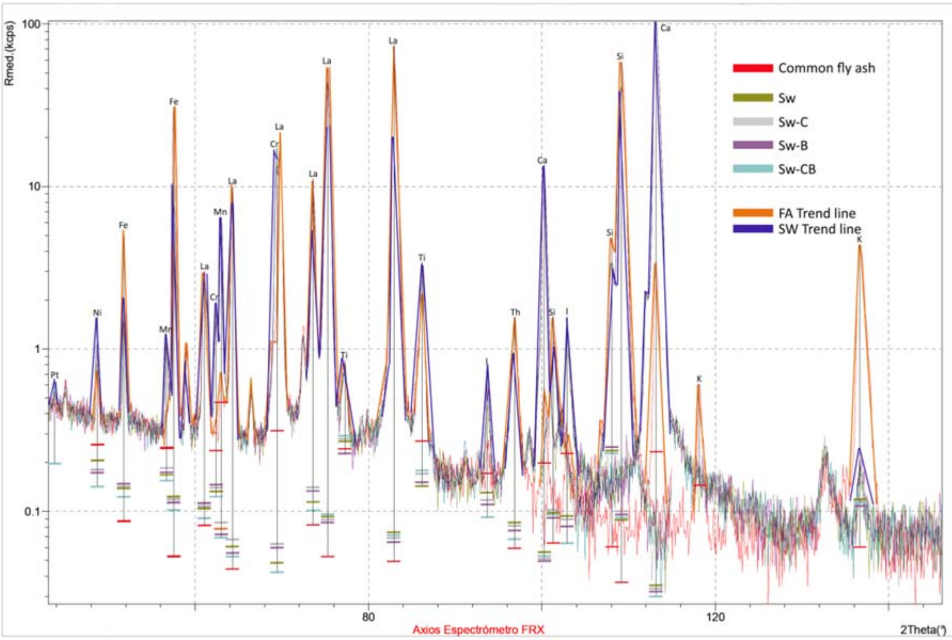


Figure 8.4: Chemical composition determination of Sw and FA through analytical technique XRF. By wavelength and certain X-ray intensity quantitative information of each sample is obtained. A trend line FA and Sw that highlights the most significant values obtained for each of these materials is shown.

Because this paper studies the application of Sw as a substitute by cement in the manufacture of building materials it is necessary obtain information about the effect on the ground water and soil, it is of more interest to know the concentrations of those environmentally relevant components which can be leached out. The study of heavy metals was carried out by the procedure EN 12457-3. This method consists of a two-step batch leaching test that uses a solution of 175 g of dry sample of the material, two liquid/solid ratios (an L/S of 2 and an L/S of 10) and deionised water as a leaching fluid. This method involves stirring the solution in two steps. In the first step, the solution is shaken for 6 ± 0.5 h with an L/S of 2, and the second step uses the same fraction with stirring of the solution for an additional 18 ± 0.5 h, after having added water to obtain an L/S ratio of 10. In both stages, the samples were left to decant, and the pH, conductivity and temperature were measured. The solution was filtered using a membrane filter (0.45 µm), and a subsample of the leachate was taken for each material. The test is performed at natural pH. Elemental concentrations were determined in the laboratory using inductively coupled plasma mass spectrometry (ICP-MS). The analysis of the leaching behaviour of the tested materials is focused on the measurement of the elements regulated by the EU Landfill Directive: ten heavy metals (As, Pb, Cd. Cr, Cu, Hg, Ni, Zn, Ca, Mg, Se and Sb) and sulphate ion. According to that European document, a residue can be classified as an inert, non-hazardous or hazardous material.

Table 8.4 shows the classification of each material sample studied by comparing them with established legal standards for heavy metal concentration. All samples were classified as non-hazardous.

Table 8.4: Concentrations of metals and sulphate on leachate at L/S=10 L/kg and L/S=2 L/kg and classification according to concentration on heavy metals. *Inert value limits exceeded are given in bold, while non-hazardous limits exceeded are underlined.*

	Metals (mg/kg)								Classification
L/S=2	**Cr**	**Ni**	**Cu**	**Zn**	**Se**	**Mo**	**Cd**	**Ba**	
Sw-N	**1.0089**	0.0021	0.0016	0.0123	0.0114	**0.6199**	0.0006	2.9060	Non hazardous
Sw-C	**1.1953**	0.0016	0.0027	0.0150	0.0173	**0.5906**	0.0008	1.3885	Non hazardous
Sw-B	0.0055	0.0001	0.0000	0.0106	0.0000	0.0130	0.0000	3.7922	Inert
Sw-CB	0.0001	0.015	0.0000	0.63	0.0001	**1.793**	0.0000	9.6688	Non hazardous
L/S=10	**Cr**	**Ni**	**Cu**	**Zn**	**Se**	**Mo**	**Cd**	**Ba**	
Sw-N	**3.9874**	0.0006	0.0041	0.0886	0.0486	**1.3015**	0.0011	4.1063	Non hazardous
Sw-C	**4.7040**	0.0014	0.0065	0.0925	0.0317	**1.2858**	0.0014	1.7157	Non hazardous
Sw-B	**9.108**	0.0000	0.0011	0.0399	0.0	**7.5493**	0.0083	4.3445	Non hazardous
Sw-CB	**6.283**	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	14.867	Non hazardous

Due to the high chromium values obtained by the leaching test and the results shown in studies [37] in which the chromium values exceed the limits established by law. A study of the amount of this metal present in Sw was performed because regulations limit the presence of water-soluble Cr VI in cement. Through this test, the amount of water-soluble Cr VI in cement was determined. In this work, replacing cement by Sw with unknown characteristics was conducted; therefore, this test should be performed to assess and verify that this new cement does not exceed the established limits for Cr VI. The procedure developed was as follows: A mortar with standard sand and the new established proportions (cement - Sw) was manufactured. These mortars were filtered, and the filtrate was treated with diphenylcarbazide and acidified within a narrow pH range. Finally, a red-violet solution was formed whose absorption was measured spectrophotometrically at 540 µm, and the content of water-soluble Cr VI was determined using a calibration curve. The results are shown in Table 8.5.

Although the material was shown to have very high levels of chromium in previous studies, it does not appear as Cr VI, so the application of this slag in cement production is possible without exceeding the limits required by law.

Table 8.5: Cr VI values

MATERIAL	Cr VI content (%)	Regulatory limit	Test method
Sw-N	0.00005		
Sw-C	0.000093	0.0002%	**UNE-EN 196-10**
Sw-B	0.00015		
Sw-CB	0.000099		

8.3.- Experimental program

A total of 16 cement mixes were made with the six types of materials (OPC, FA, Sw-N, Sw-C, Sw-B and Sw-CB) and the 10%, 20% and 30% of the replacement ratio. Four types of processed Sw were characterized to establish dosages. Then, mechanical behaviour tests were performed. The mechanical performance and durability were tested for six experimental replicates of each sample (Table 8.6).

Mixture and dosage

A mortar sample (control) with a mix proportion of 0.5:1:3 (water; cement; sand) was designed as the control mix. To compare Sw with cement made using a common addition, three sets of cement with FA were manufactured with different substitution percentages (10%, 20% and 30%).

The wastes were then used as substitute for cement at different replacement levels (10%, 20% and 30%) for the manufacture of mortar. Table 8.6 shows the different quantities of materials applied in the mixtures used for this performance.

The method used for the design of the dosages was set according to UNE-EN 196-1. The mortar control was set with dosage according to this standard.

Table 8.6: Mortar mix proportions

		DOSAGE (g)					
		NS	**FA**	**Sw-N**	**Cement**	**Water**	**%Cement**
Control	Control – OPC	1350	-	-	450	225	25
	Control – FA10	1350	45	-	405	225	22.5
Series 1 (10%)	S10-Sw-N	1350	-	45	405	225	22.5
	S10-Sw-C	1350	-	45	405	225	22.5
	S10-Sw-B	1350	-	45	405	225	22.5
	S10-Sw-CB	1350	-	45	405	225	22.5
	Control – FA 20	1350	90	-	360	225	20
Series 2 (20%)	S20-Sw-N	1350	-	90	360	225	20
	S20-Sw-C	1350	-	90	360	225	20
	S20-Sw-B	1350	-	90	360	225	20
	S20-Sw-CB	1350	-	90	360	225	20
	Control – FA 30	1350	135	-	315	225	17.5
Series 3 (30%)	S30-Sw-N	1350	-	135	315	225	17.5
	S30-Sw-C	1350	-	135	315	225	17.5
	S30-Sw-B	1350	-	135	315	225	17.5
	S30-Sw-CB	1350	-	135	315	225	17.5

Experimental methods

This study was conducted to determine the mechanical properties and durability characteristics of mortar prepared with stainless steel slag waste. Therefore, samples with different substitution percentages for the manufacture of cement mortar were created to analyse the cement capacity of the stainless steel slag waste, to evaluate the influence of waste processing on the mechanical behaviour of mortars and to determine the optimal replacement ratio for increasing the economic value of this waste, different percentages of Sw processed described above including 10%, 20% and 30%, were applied. Thus, it is possible observe how the properties of the cement manufactured with Sw differ from those of cement without additions (Control-OPC) and cement with a common addition (Control-FA).

The hardened mortar was characterised according to six properties: dry bulk density, porosity, water absorption, compressive and flexural strength and dimensional instability (shrinkage). Six samples of each specimen were evaluated. Table 8.7 shows the testing standard used.

The dry bulk density and water absorption due to capillary were measured at 28 days according to Standard indicated in Table 8.7. Porosity was measured through the following procedure: the weight right after curing and the weight after 24 h in an oven at 105 °C were measured; porosity is the ratio between the loss of weight and the initial weight; the result is expressed as a percentage.

To observe the corresponding pores of the material a Scanning Electron Microscopy (SEM) at 28 days was used. The signals generated during analysis produce a two-dimensional image and reveal information about the sample including external morphology (texture).

The compressive and flexural strengths were measured at different ages (1, 7, 28 and 90 days) according to UNE-EN 196-1. A hydraulic press was used to apply a load at a constant speed. In relation to the determination of the dimensional stability the specimens were first cured at a room with 20 ± 1°C and 95 ± 5% relative humidity for 3 days. Then the specimens were installed on the measuring device for drying shrinkage at a room with 20 ± 1°C and 65 ± 5% relative humidity. The drying shrinkage of the mortar was measured continuously for 90 days.

Table 8.7: Mortar characterisation test

	Test method	Dimension of specimens	Curing time
Properties of hardened mortar			
Dry bulk density and porosity	UNE-EN 1015-10	Prismatic 40 × 40 × 160 mm	28 days
Water absorption due to capillary	UNE-EN 1015-18	Prismatic 40 × 40 × 80 mm	28 days
Flexural strength	UNE-EN 196-1	Prismatic 40 × 40 × 160 mm	1, 7,28, 90 days
Compressive strength	UNE-EN 196-1	Prismatic 40 × 40 × 80 mm	1, 7,28, 90 days
Shrinkage	UNE 83831	Prismatic 40 × 40 × 160 mm	1, 7, 14,28, 56, 90 days

Multivariate analyses

In order to characterize as whole mechanical and durability properties of use of stainless steel slag waste in cement, multivari ate analysis were applied on the following parameters: flexural strength (FS), compressive strength (CS), and shrinkage (SH), because they are the main parameters to evaluate the possibility of using new cements [38]. A multivariate factor analysis was performed on the results of parameters used at 28 days for FS and CS, and at 90 days for SH from cement mortar mixes studied (Table 8.6) in order to determine the degree of association and/or discrimination among them. The date selected to evaluate FS and CS was based according to cement standards UNE-EN 196-1; however, SH was analysed when the mortar cement mixes did not present dimensional changes (Figure 8.10). Analyses were carried out using Rv. 3. 1. 1. (R Foundation for Statistical Computing, http://www.Rproject.org/). Prior to analysis, the normality of the data was checked using a normality test for multivariate variables using the package 'mvnormtest' [39]. Factor analysis was performed by a decomposition of the data matrix among populations in a Q-mode type analysis using the principal function implemented in the package 'psych' [40]. This analysis produced a set of variables (factors) that are linear combinations of the original variables. The new factors are independent of each other and ranked according to the amount of variation accounted for. After the initial extraction by the principal method, an orthogonal varimax raw rotation was used to estimate the factor loadings. Only factors with SS (sum of squares) loadings > 1 were extracted.

Multivariate analysis of variance (MANOVA) with the canonical option was performed on the cement mortar mixes studied (Table 8.6) to determine the differentiation among them and to estimate significant differences between them using pairwise comparison. The analysis was based on the mechanical and durability parameters including CS, FS and SH. Additionally, the results of the studied parameters were subjected to univariate analysis of variance (ANOVA), and their mean values were compared using Tukey's test [41] for p _ 0.05 using the general model procedure of SAS (Statistical Analysis System v. 9.4; SAS Institute, Cary, NC, USA).

8.4.- Results and discussion

Density, porosity and water absorption of hardened mortars

Physical properties including density, porosity and absorption parameters were studied for the mortars hardened for 28 days.

As in previous studies [42], it was observed that the apparent density of the cement with only FA was lower than that of the OPC control, as shown Table 8.8. Furthermore, Table 8.8 shows that the use of Sw in cement mortar mixtures can considerably increase the mortar's unit weight due to its higher density compared to natural slag [43] or other types of waste with lower densities [44]. Therefore, the change in this property is conditioned for the physicochemical characteristics of the Sw with irregularly shaped porous grains of various sizes. In addition, cement mortar mixes containing processed Sw showed lower density values than those samples manufactured with unprocessed Sw. This decreasing trend in density can be explained by analysing the characterization results of the materials (Table 8.2), in which Sw that was crushed and burned showed a decrease in density compared to Sw-N.

Table 8.8: Density, porosity and water absorption of hardened mortars

		Dry bulk density (kg/dm^3)	**Porosity (%)**	**Water absorption ($kg/m^2·min^{1/2}$)**
Control	Control – OPC	2.09	18.88	1.98
	Control – FA10	2.03	21.37	2.51
Series 1 (10%)	S10-Sw-N	2.56	19.17	2.16
	S10-Sw-C	2.41	19.12	2.07
	S10-Sw-B	2.33	19.14	2.06
	S10-Sw-CB	2.27	19.06	1.98
	Control – FA 20	2.02	21.42	2.78
Series 2 (20%)	S20-Sw-N	2.61	20.26	2.36
	S20-Sw-C	2.55	20.17	2.32
	S20-Sw-B	2.49	20.21	2.26
	S20-Sw-CB	2.41	20.11	2.22
	Control – FA 30	1.97	21.89	2.86
Series 3 (30%)	S30-Sw-N	2.67	20.77	2.62
	S30-Sw-C	2.61	20.62	2.53
	S30-Sw-B	2.53	20.73	2.49
	S30-Sw-CB	2.48	20.53	2.42

According to Table 8.8, the OPC mixture has a lower porosity, and the samples with FA have a higher porosity. The amount and size of pores (porosity) are affected by hydration products and pozzolanic materials that fill the voids in the cement paste [42]. As expected, the use of highly porous slag as FA considerably increases the porosity of the mortars produced. However, the voids of blended cement mortar containing Sw replacement were lower than those of the FA mixture but tend to increase with increasing Sw replacement. On the other hand, analysing the effects of the processed stainless steel slags, Table 8.8 shows that the processed Sw decreased porosity relative to the unprocessed slag (Sw-N); the lowest porosity values were obtained when the slag was burned and crushed (Sw-CB).

Based on the above results, water absorption is an extremely important property for mortars (Table 8.8), as they are usually exposed to environmental phenomena. As a consequence, an inappropriate mortar could become damaged and cause efflorescence phenomena [45]. The pores are formed in the binder matrix during the hydration and setting process or due to the removal of water during hardening. Over time, the pores are reduced, leading to the onset of secondary changes such as shrinkage phenomena [46].

Water absorption has a direct relationship with the voids, so the absorption decreased as the voids decreased. As shown in Table 8.8, the mortars manufactured with Sw presented water absorption values higher than the control, similar to the porosity values. The use of FA as an addition in the manufacture of cement mortars increased the water absorption with respect to the control OPC and the Sw addition. This result was also obtained in previous studies [47,48]. Similar to the porosity values, processed slag showed lower water absorption than the unprocessed slag. Therefore, the obtained results show that water absorption has a direct relationship with the voids, i.e., the absorption decreased as the voids decreased. However, the decreasing of pores and absorption is not significantly matched with an increase in density. The new additions (Sw) present a high specific weight, and incorporating Sw into the cement increases the density of the hardened mortars [49].

The porosity of the material was observed using scanning electron microscopy (SEM) at 28 days. Figure 8.5 shows high-resolution images of the fracture surfaces of different samples. Microscopic observations revealed that the specimens with FA had spherical pores with large diameter that were probably due to the evaporation of water; these findings are in agreement with the recorded porosity values. However, the cement mortars with the addition of Sw did not present large pores. The presence of voids decreased in mortars containing processed Sw, as shown in Figure 8.5, in which the presence of pores in S10-Sw-CB was similar to that of the Control-OPC mortar. Increasing the percentage of Sw in the manufactured mortars led to an increased number of pores.

The analysis of the images obtained by scanning electron microscopy revealed the appearance of a major microstructure such as crystals in the mortars manufactured with SW (letter b Figure 8.5). The crystal had the hexagonal and flake characteristic of $Ca(OH)_2$. The appearance of this type of crystal was observed in all mortars that were manufactured with different percentages and different treatments of Sw, but it was more abundant in mortars with a higher percentage of Sw.

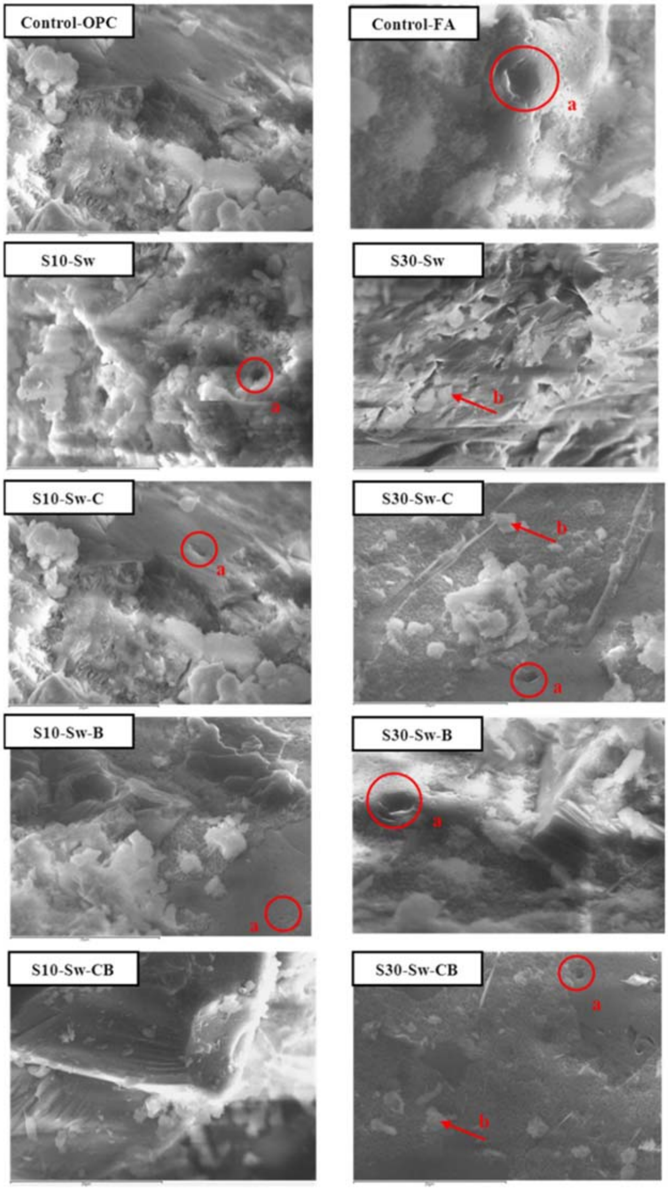


Figure 8.5: Micromorphology of cement mortars. (a): Pores in the hardened mortars at 28 days; (b): Crystals of $Ca(OH)_2$

Compressive and flexural strength of hardened mortar

To evaluate the mechanical behaviour of the manufactured cement mortars, compressive and flexural strength tests were performed according to UNE-EN 196-1. Table 8.9 shows the results for the compressive and flexural strength of the different types of mortars made. The compressive strength progressively increased with time. An increase was observed with increasing curing age (Figure 8.6).

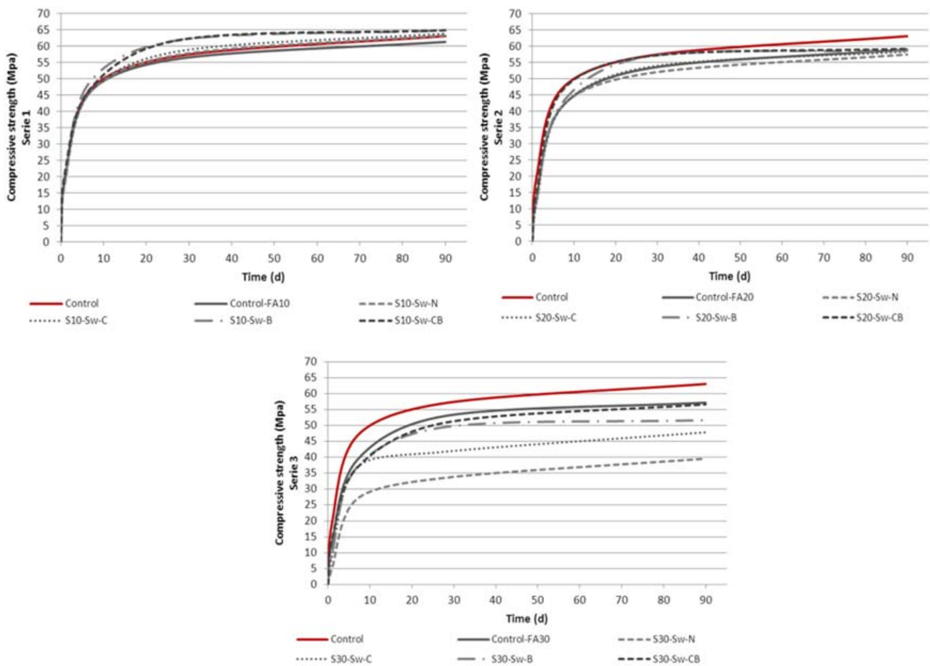


Figure 8.6: Compressive strength evolution along time of Control mortars (OPC and FA) and different replacement ratio of Sw (S1, S2 and S3).

Series 1 with 10% replacement demonstrated compressive strengths higher than or close to that of the control OPC. These results were similar to those of other studies conducted on the use of waste as a substitute for cement [50] demonstrated that when MSWI-LED slag was used to replace 5–

20% of the cement, a compressive strength was obtained that was greater than or close to that of the control OPC. Tsakiridis et al. [51] studied the use of steel slag for Portland cement clinker production and found that a 10.5% addition of steel slag did not negatively affect the quality of the cement produced. Monshi and Asgarani [52] produced a type of cement from steel slag (with 8%), iron slag and limestone that satisfied the requirements for compressive strength of type I Portland cement. This demonstrates that when using stainless steel slag waste in cement production, its addition amount is usually very small to ensure the essential strength requirement of the concrete. The highest compressive strength results were obtained in mortars made with processed Sw. Using Sw-CB improved the compressive strength at 28 days in Series 1 by 8.5% compared to the control OPC. These results demonstrate the activation of slag using simple processes such as grinding and burning. Kriskova et al. [13] found that mechanical activation significantly increased the reactivity of steel slag.

Table 8.9: Compressive and flexural strength of hardened mortar

		Age (Days)					Age (Days)				Bi (kg.m^{-3} /MPa)
		1	7	28	90		1	7	28	90	
Control - OPC	**Compressive strength (MPa)**	19.68	46.74	57.03	63.03	**Flexural strength (MPa)**	5.07	8.85	11.09	13.01	2.50
Series 1 (10% replacement of cement)											
Control-FA10	**Compressive strength (MPa)**	19.56	46.12	56.16	61.24	**Flexural strength (MPa)**	5.47	7.23	12.23	14.16	2.29
S10-Sw-N		18.24	46.01	57.37	63.23		4.64	6.50	12.12	14.08	2.25
S10-Sw-C		18.96	46.13	57.47	63.78		6.11	9.68	12.50	14.14	2.24
S10-Sw-B		19.65	48.37	58.64	64.72		6.39	9.69	12.58	14.58	2.19
S10-Sw-CB		21.47	47.06	61.87	64.81		6.30	9.04	12.8	14.24	2.08
Series 2 (20% replacement of cement)											
Control-FA20	**Compressive strength (MPa)**	13.49	41.15	53.16	58.93	**Flexural strength (MPa)**	4.86	7.67	11.21	13.56	2.14
S20-Sw-N		12.26	41.28	51.64	57.39		3.28	7.25	10.79	13.39	2.21
S20-Sw-C		11.54	41.10	53.55	58.28		4.57	7.73	10.83	13.64	2.13
S20-Sw-B		12.48	41.36	54.60	58.61		4.79	7.39	11.01	13.79	2.09
S20-Sw-CB		14.85	46.04	56.92	59.14		4.24	8.15	11.52	13.84	2.00
Series 3 (30% replacement of cement)											
Control-FA30	**Compressive strength (MPa)**	13.41	39.15	52.97	57.15	**Flexural strength (MPa)**	4.15	7.48	11.17	13.06	1.88
S30-Sw-N		5.28	26.88	33.55	39.50		1.55	8.07	9.58	10.21	2.98
S30-Sw-C		9.07	36.78	41.73	47.80		2.26	7.28	9.55	10.14	2.39
S30-Sw-B		9.87	36.91	47.49	51.63		2.7	8.16	9.63	11.48	2.11
S30-Sw-CB		14.51	36.71	50.86	56.60		3.77	8.13	10.56	12.17	1.97

In contrast, the compressive strength decreased compared to the control OPC in series 2 and 3 with increasing Sw for all ages and all series (Table 8.9 and Figure 8.7). The smaller compressive strength losses occurred in processed Sw. The crushed and burned slag had lower values of loss relative to the control. A 0.2% loss in compressive strength was observed for the S20-Sw-CB, and a 10.8% loss was observed for S30-Sw-CB. Figure 8.8 shows that Sw-B and Sw-CB did not show any correlation between the compressive strength and the replacement rate because these materials showed higher strength than the control mortar (0% replacement rate).

On the other hand, comparing mortars containing Sw with the control mortars manufactured with FA for series 1 and 2, higher compressive strength values were obtained for mortars containing processed Sw (Sw-C, Sw-B and Sw-CB). However, when the replacement was 30%, the control FA mortars obtained higher values of compressive strength compared to the manufactured Sw.

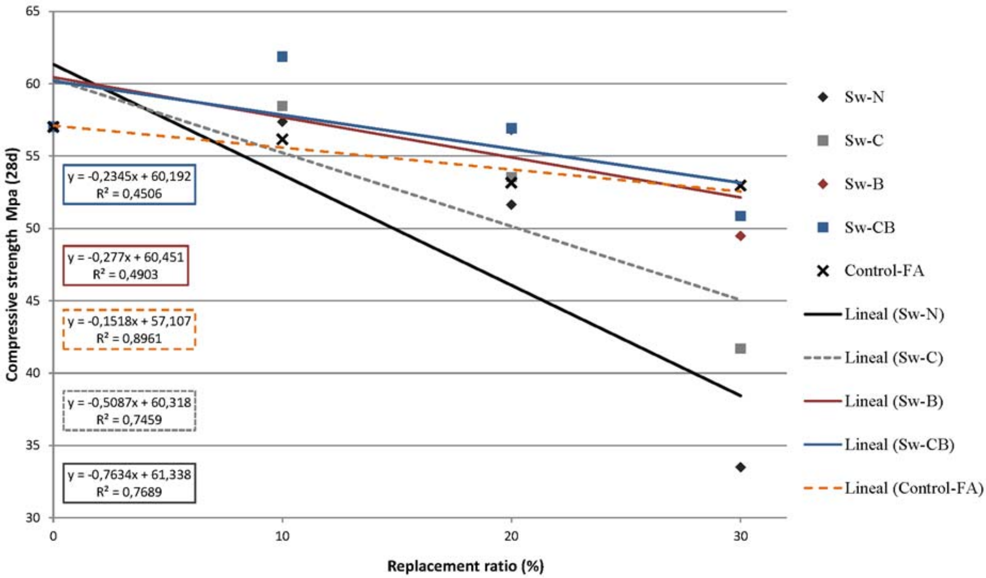


Figure 8.7: Comparison between compressive strength at 28 days and replacement ratio according to the type of treatment given to Sw (Sw-N, Sw-C, Sw-B and CB-Sw).

Significance = F probability of main effects in regression analysis, according to Tukey´s test for $P \leq 0.05$.

The use of Sw causes a reduction of binder content in cementitious a system which is an effective way to mitigate environmental impacts without increasing costs. To evaluate the effect of content binder on bond strength of cement mortar interface, the efficiency use of binder was measured by the binder intensity indicator (bi) proposed by Damineli et al. [53] which measures the total amount of binder necessary to deliver one unit of a given performance indicator which compares the total consumption of binder materials in kg/m^3 and the performance requirement. In this paper, it was measured the amount of binder required to achieve 1 MPa of compressive strength at 28d of mortars.

Based on the data shown in Table 8.9 it can be concluded that the best indexes were obtained for S30-Sw-CB mortars made with the use of 100 kg/m^3 cement. Slightly less favourable was the use of Sw-CB for series 2. The least satisfactory results were obtained with a larger amount of cement (129 kg/m^3), in case of the series 1 with 10% of replacement.

Similar to the values obtained from compressive strength, the flexural strength decreased with increasing substitution percentage of Sw (Table 8.9). These results are corroborated by previous works [54, 55] in which the flexural strength of manufactured mortars with different waste as a substitute for cement decreased with increasing substitution percentage.

Dimensional instability (shrinkage)

To determine the optimal Sw replacement it is necessary to evaluate the dimensional instability produced in cement mortar mixtures. A shrinkage study was performed over a long time. The results show a similar trend in the linear shrinkage (µm/m) over time (Figure 8.8). This figure shows that the total drying shrinkage of cement mortars with 10% Sw at 90 days are very close to each other; in addition, they all have values near those of Control-OPC and Control FA-10.

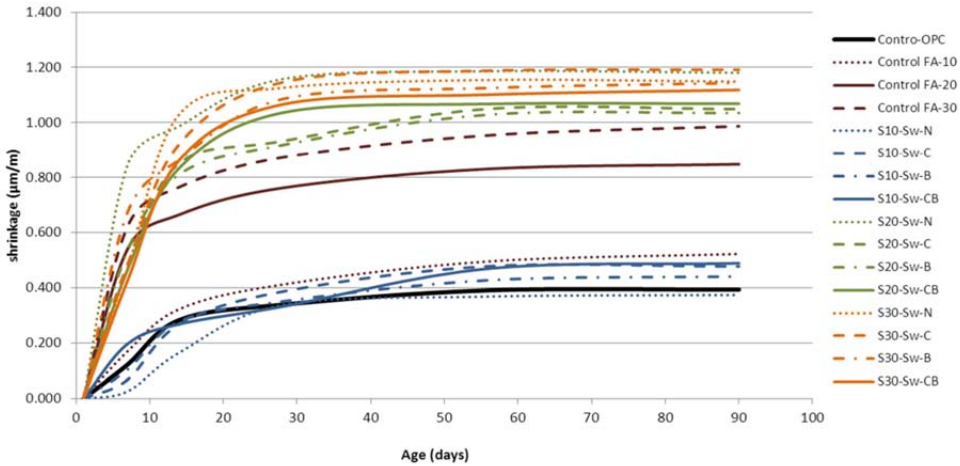


Figure 8.8: Shrinkage of the mortar as a function of age in days.

The shrinkage values obtained for Sw cement mortars were similar to those obtained in previous studies [56, 57] where shrinkage was similar to or lower than that of control OPC cement in mixes with a minimum substitution percentage in the manufacture of cement and concrete with steel slags. However, the results obtained in this study differ from those obtained in previous works. In cement mortars made with 20% and 30% Sw, the shrinkage values increased significantly, as shown in Figure 8.8. Q.Wang et al. [57] obtained a greater shrinkage for concrete manufactured with 15–30% steel at early ages (seven days), but at 90 days, this shrinkage was similar to that obtained for a control OPC. The dimensional changes are due mostly to the porosity of the material [58] according to the degree of substitution in the manufacture of cement mortars. As the substitution percentage increases, a higher correlation between porosity and shrinkage is observed, as shown in Figure 8.9.

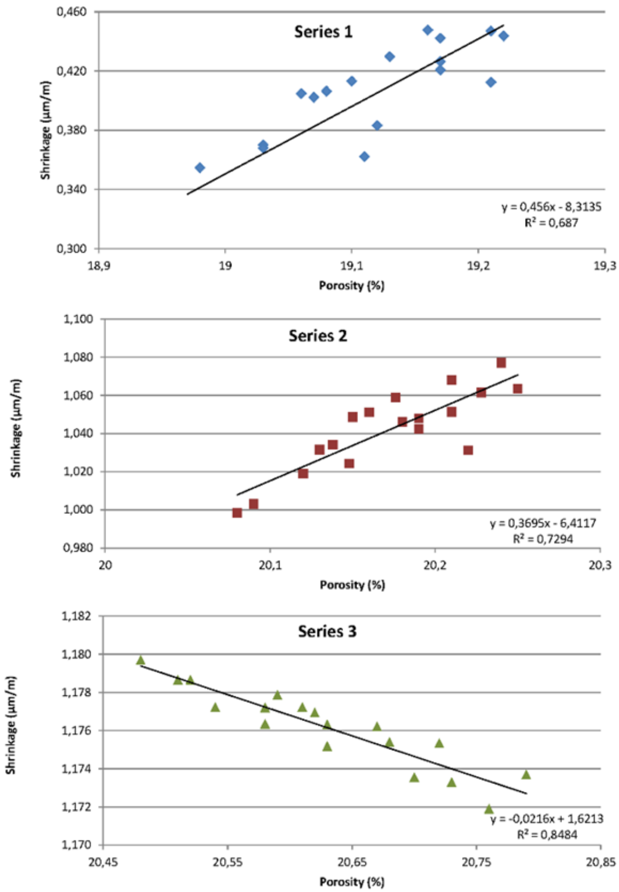


Figure 8.9: Relationship between between shrinkage and porosity parameters at 28 days.

Significance = F probability of main effects in regression analysis, according to Tukey´s test for *P ≤0.05*.

The dimensional changes noted in the Sw cement mortar specimens can be attributed to the chemical composition of the stainless steel slag, which basically consists of calcium carbonate that expands when it absorbs water [58]. Due to the loss of absorbed water during the first days of curing, cement mortars manufactured with stainless steel slag present a high porosity (Table 8.8 and Figure 8.5) and experience shrinkage (Figures 8.8 and 8.9).

Multivariate analyses on mechanical and durability properties of stainless steel slag waste in cement mortar

In the factor analysis, the first two factors (Sum of Squares (SS) loadings > 1) accounted for 96.2% of the total variance of the mechanical and durability parameters of the cement mortar mixes analysed (Table 8.10). Table 8.10 includes the SS loadings for the two factors extracted, which were a linear combination of all of the parameters in the analysis. The eigenvectors for each parameter were used to interpret the mechanical and durability meaning of the factors. Factor 1 was dominated by a high negative weight (eigenvector = -0.923) for SH, relating this factor to durability (Table 8.10 and Figure 8.10A). Factor 2 was dominated by a high positive (eigenvector = 0.919) for CS, thereby relating this factor to mechanical strength (Table 8.10 and Figure 8.10A). On the other hand, FS was not highly associated with any of the factors extracted but, to a lesser extent, showed a negative weight to Factor 1 (eigenvector = -0.710) and a positive weight (eigenvector = 0.650) to Factor 2 (Table 8.10 and Figure 8.10A). The results of factor analysis were graphically represented in Cartesian plots in which the cement mortar mixes included in Table 8.10 were projected on the x- and y-axes, respectively, as pairwise combinations of Factors 1 and 2 (Figure 8.10B). With few exceptions, replicated samples of each cement mortar mixes were close except for those of S10-Sw-C and S20-Sw-C, which showed a wide distribution for the combinations of both factors due to the variability of their parameters results because of systematic errors due to the non-uniformity of mortars or changes in line voltage, temperature or mechanical vibrations of the equipment used.

Table 8.10: Eigenvector and SS loadings of factor derived from mechanical parameters and shrinkage for cement mortar mixes from combination between several steel slag waste (Sw) treatments and cement replacement ratios as well as control mortar mixes. Values of morphometric factors 1 to 2 (eigenvector >0.71) are underlined.

	Principal component	
Mechanical parameters	**F1**	**F2**
CS	0.373	0.919
FS	-0.710	0.650
SH	-0.923	-0.352
SS loadings	1.495	1.391
% of total variance	49.80	46.40
Cumulative % of total variance	49.80	96.20

According to their relative position along the x-axis (Factor 1) on Figure 8.10B, the SH increases and FS decreases slightly from right to left, basically grouping cement mortar mixes with low material durability (>SH) at the left position (Figure 8.10B). According to their positions along the y-axis on Figure 8.10B (Factor 2), the CS increases and FS increases slightly from bottom to top along the y-axis, grouping cement mortar mixes with high mechanical strength (>CS and FS) at the top position (Figure 8.10B). Then, when projected on the plane of Factors 1 and 2 on Figure 8.10B (96.2% of the total variance), cement mortar mixes with a high mechanical strength and material durability are located at the right-top quadrant, including mortar samples with a 10% replacement ratio of cement (S10-Sw), with a clear distinction between stainless steel slag waste that was processed (Sw-C, Sw-B and Sw-CB) and unprocessed (Figure 8.10B).

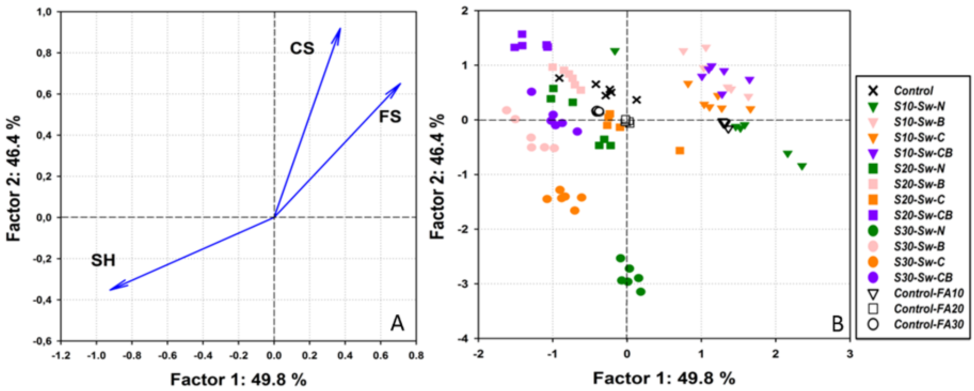


Figure 8.10: Factor Analysis (FA) of mechanical parameters and shrinkage analyzed to evaluate the use of Sw with different treatments in the manufacture of cement mortars. Left panel: projection of parameters on the plane of factors 1 and 2 (A). Right panel: projection of cement mortar mixes on the plane of factors 1 and 2 (B). Abbreviations: CS = compressive strength, FS = flexural strength, SH = shrinkage.

Conversely, mortar samples with a low mechanical strength and material durability are located at the left-bottom quadrant, including mortar mixes with a 30% replacement ratio (S30), showing a clear distinction between mortar mixes crushed stainless steel slag waste (Sw-C) and burned stainless steel slag waste (Sw-B) (Fig. 7.10B). Mortar samples with this replacement percentage of unprocessed waste (S30-Sw-N) are located in the bottom quadrants below x = 0, resulting in cement mortar mixes with moderately high material durability but with a low mechanical resistance. In addition, the combination of burning and crushing treatments at this replacement ratio (S30-Sw-CB) resulted in these mortar samples being located at the middle part of the plane left of y = 0 (Figure 78.10B). On the other hand, cement mortars with a high mechanical strength but a low material durability are located at the left-top quadrant, including most of the mortar mixes with a 20% replacement percentage, showing a clear distinction between burned and burned-crushed Sw (S20-Sw-B and S20-Sw-CB) (Figure 8.10B). However, S20-Sw-C and S20-Sw-N mortar mixes were located in the left quadrants above and below y = 0 and around y = 0 and x = 0, respectively (Figure 8.10B). Common fly ash control mortar samples with 20% and 30% replacement (Control-FA20 and Control FA30, respectively) were also located in the centre part of the plane and were closely grouped (Figure 8.10B). In contrast, the Control-FA10 samples were located in the middle part of plane to the right of y = 0 and were closely grouped with the rest of the S10 cement mortar mixes analysed (Figure 8.10B).

Multivariate analysis of variance (MANOVA) was performed on the cement mortar mixes studied and showed a significant effect on the mechanical and durability properties when using stainless steel slag waste as a replacement for cement in mortars (Wilk'Lambda = 0.00057, F = 58.74, $P < 0.0001$). In this sense, when projected on the plane of Factors 1 and 2, a wide spatial separation was observed among the most manufactured mortars, particularly between the different series with cement replacement (Figure 8.10B).

This spatial discrimination was more significant with increasing replacement percentage, showing an increased discrimination between waste treatments in the S30 series (Figures 8.7 and 8.10B).

These differences were mostly related to compressive strength (Figure 8.10B), resulting in significant differences in this parameter between all of the Sw treatments studied ($P < 0.05$). These differences could be due to the influence of physical characteristic alterations (Table 8.2) in the mechanical properties due to using Sw in the hardened cement mortar. In addition, the physical characteristics of each Sw treatment directly affected the durability. This fact is clearly shown in the study of the porosity properties because the mortars with a high percentage of Sw showed increased shrinkage values (S30; $R^2 = 0.848$, $P < 0.05$), as described by Arandigoyen (2005) [59] (Figure 8.10). On the other hand, Control-OPC can be clearly differentiated from the mortar mixes when the cement was replaced by 10% and 30% of waste by-product in contrast to the samples with a 20% replacement ratio (Figure 8.10B); however, pairwise comparisons among Control-OPC and different series showed highly significant differences in all combinations ($F \geq 11.42$, $P < 0.0001$). All of the common fly ash controls were also clearly differentiated from Control-OPC on the plane (Figure 8.10B). In addition, pairwise comparison analyses among the common fly ash controls with respect to its replacement series were significantly different in all combinations ($F \_ 8.92$, $P < 0.0001$).

Overall, multivariate analyses demonstrated that replacement rates higher than 20% Sw in the manufactured mortars did not produce any improvement in the mechanical and durability properties except when the waste was crushed and burned (S30-Sw-CB), as shown by the similar values of mechanical behaviour as compared with the control samples (Table 8.10 and Figure 8.10B). Nevertheless, in the case of series S10 and S20, an increase was observed for the CS and SH parameters in Sw-B and Sw-CB with respect to Sw-N ($P < 0.05$), indicating that crushing and the combination of both burning and crushing improved the mechanical and durability properties.

8.5.- Conclusions

This research evaluates the properties and characteristics of stainless steel slag waste for the manufacture of mortars and the mechanical and environmental properties of these mortars to identify whether the replacement ratio significantly affects the measured properties.

The following conclusions were obtained:

- Sw and Sw-C present high absorption and density. These values decrease when the stainless steel slag is crushed; a suitable particle size distribution was obtained for both materials, so it is possible to use both as a substitute for cement.
- In terms of the chemical properties, stainless steel slags have high values of metal oxides similar to those present in conventional fly ash. These values result in positive cementitious capacity in the waste.
- Regarding the physical and mechanical properties, replacing cement with stainless steel slag waste increases the compressive and flexural strength if the substitution percentage is 10%; these values are further improved if the stainless steel slag waste is crushed. For

mortars with this waste percentage, the reactions are similar to those of the control mortar.

- However, with increasing percentage of stainless steel slag, the mortar's resistance to compression and flexural decreases, and its shrinkage increases. If 30% of the cement is replaced by Sw-C, the compressive strength decreases by less than 25% compared to the control, but if the stainless steel slag is not processed, this compressive strength is smaller.
- Finally, our study confirmed that multivariate analysis is a useful tool for classifying wastes according to its durability, mechanical behaviour and environmental impact because it can evaluate and select quality indicators related to the use of different waste types.

In conclusion, replacing cement with stainless steel slag waste for the manufacture of mortar improves the mechanical properties up to a certain degree of substitution. This use can provide some value to the large amount of waste produced and reduce the consumption of raw materials.

This study showed that replacing up to 20% of cement with crushed Sw is recommended. Cement mortar mixes manufactured with 20% Sw-C obtained values similar to those of Control-OPC. On the other hand, for substitution over 20%, this study recommends a combined process of crushing and calcination.

8.6.- Acknowledgments

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CAPÍTULO IX

PHOSPHOGYPSUM TREATED TO BE USED AS ALTERNATIVE SET REGULATOR AND MINERAL ADDITION IN CEMENT PRODUCTION

Rosales J., Pérez S.M., Cabrera, M., Gázquez M.J., Bolívar J.P., & Agrela, F.

IX PHOSPHOGYPSUM TREATED TO BE USED AS ALTERNATIVE SET REGULATOR AND MINERAL ADDITION IN CEMENT PRODUCTION.

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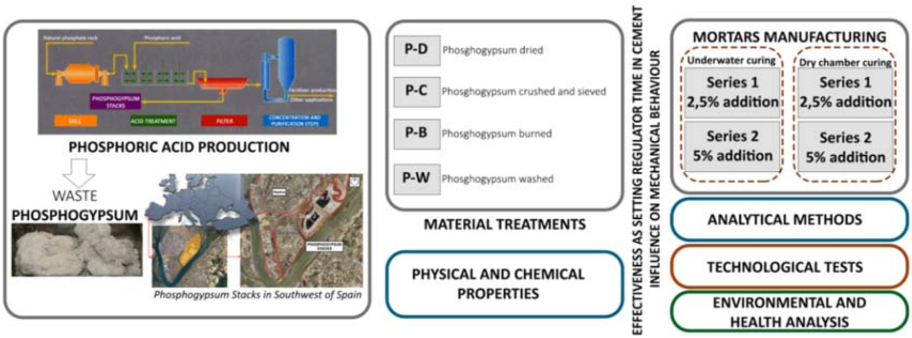

Abstract

Different treatments on phosphogypsum samples extracted in Huelva, Spain, different curing conditions and different percentage of addition were studied to evaluate the possibilities of being used as set regulator and as supplementary cement material to improve the mechanical behaviour of cement mortars.

The physical-chemical properties, mechanical behaviour and environmental impact of these phosphogypsum-based cement mortars were determined.

It was concluded that the phosphogypsum treatments and curing conditions influence the mineralogical transformations of mortars and therefore also the mechanical behaviour of the mortars tested. In addition, the heavy metal impurities in the phosphogypsum were immobilized in the cement matrix. Obtaining a clear improvement in the technical properties of cement mortars made with this waste compared to the traditional use of natural gypsum.

Keywords:

Phosphogypsum treatments, Pozzolanic addition, Curing conditions, Cement mortars, Technical properties.

9.1.- Introduction

The generation and management of any type of waste is a serious environmental problem in today's society. Thus, the reduction of its generation and its appropriate management are necessary to avoid serious impacts on the environment that can cause pollution affecting ecosystems and human health [1].

Phosphogypsum (PG) is an industrial by-product of the fertiliser industry, mainly from the production of phosphoric acid.

Approximately 250 Mt of PG are generated around the world as an inorganic by-product in several industrial processes [2, 3]. In Spain, due to the manufacture of a number of fertiliser products during the years 1968–2010, around 100 Mt of this waste are accumulated in stacks located 1 km from the city of Huelva [4].

One of the main uses of PG investigated is the application of this by-product as a fertilizer in agricultural soils [5]. Actually, only 15% of world production is used and recycled [6]. The remaining 85% is accumulated in large areas causing environmental issues [4]. The valorisation of this by-product is highly dependent on the properties of the PG and the country of origin.

The most important and motivating use of PG could be in the cement manufacturing process. In this process, PG could be used as a replacement for natural gypsum (NG) as a setting retarder [7, 8]. Based on previous works, this paper analyses the use of PG as setting-time retarder to replace NG, evaluating its properties in improving the mechanical behaviour of cement mortars. This leads to a study of the application of the PG accumulated into stacks located in Huelva, Spain and stored without recovery.

The application of different PG treatments could improve the properties of construction materials manufactured with it [9]. Treated PG can be used as an ingredient of plaster [10–12]. Higher compressive strength values of Portland cement were shown with calcined PG [13]. This is due to the structure anhydrite cement generation by heating PG at 1000 °C [14].

In addition to the mechanical properties, environmental aspects must be considered, due to the presence of impurities in the stored PG [15–17]. The impurities are of different origin depending on the phosphate rock used as raw material and the manufacturing processes used [18]. The PG contains 5–6% impurities, which can be heavy metals, radionuclides or fluorides [19]. The impurities present in the PG affect directly the mechanical properties of cement mortars manufactured with this by-product. It has been found that several impurities, such as P2O5, F or organic matter, can be removed by washing with water [11].

For this reason, and based on previous comments, the main objective of this study has been to analyse the influence of the untreated PG and of the different treatments, percentages of addition and curing conditions on the technological properties, mineralogical characteristics and environmental and health aspect of cement mortars manufactured with PG from Spain.

9.2.- Experimental program

9.2.1 - Materials

The present study evaluated representative samples of the deposits of PG located in Huelva, Spain. The samples were processed by four different treatments. First, a control sample was manufactured with clinker and natural dihydrated gypsum (Control-NG); this sample was compared to those manufactured with PG prepared by different treatments as a substitute for natural gypsum. Finally, to compare the properties of these mortars with a commercial cement, a sample was manufactured with cement CEM I 42.5R without additions (Reference-OPC).

Phosphogypsum

The processing of the material was carried out using different methods. Four types of processed PG were used in this study:

(1) dried phosphogypsum (PG-D). The material was dried in an oven for 48 hours at 40ºC.

(2) crushed phosphogypsum (PG-C). The phosphogypsum was crushed using a ball mill and subsequently sieved through a 125 µm mesh;

(3) burned phosphogypsum (PG-B). Material obtained by the calcination of phosphogypsum in a muffle at a temperature of 800 ºC for 18 h; and

(4) washed phosphogypsum (PG-W) which was washed in a beaker with distilled water in a liquid/solid ratio of 10:1. During this first wash the PG was stirred for 40 min, then left to stand for 20 min and the pH of the material was measured; finally, it was filtered with laboratory paper. A second wash was performed after filtering with the same procedure. Finally, the material was dried for 48 h in an oven at 40 °C.

The particle size distribution was determined using wet laser diffraction (Malvern Mastersizer). Figure 9.1 shows the morphology of the material particles and the variations in particle shape and size.

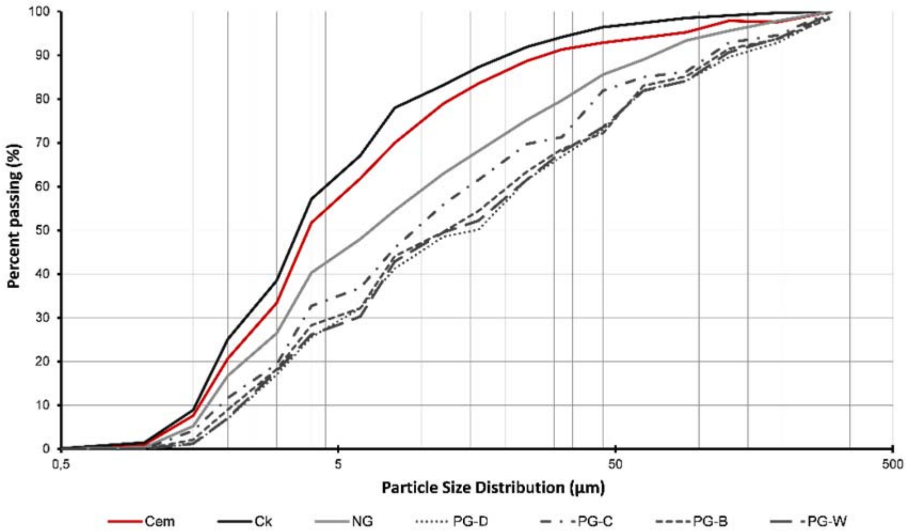

Figure 9.1: Particle size distribution of the different PG treatments compared to Cem, Ck and NG.

The particle distribution of the material was fundamentally dependent on the type of phosphate rock used as raw material and by the conditions of the manufacturing process [20, 21]. Regarding the four types of materials obtained in the laboratory, PG-C showed a finer particle distribution due to the crushing process to which it had been subjected.

The chemical properties of the different PG samples are summarized in Table 9.1.

Table 9.1: Chemical composition of raw materials (wt%)

PROPERTIES			Cem	Ck	NG	PG-D	PG-C	PG-B	PG-W
Elemental content (%)	**Si**	*UNE-EN 196-2:2014*	7.78	8.40	2.98	0.40	0.38	0.55	0.47
	Ca		48.2	49.3	23.3	22.5	22.8	27.7	23.1
	K		0.28	0.26	0.08	-	-	-	-
	Mg		0.49	0.42	0.37	-	-	-	-
	Fe		3.53	3.78	0.07	0.03	0.04	0.04	0.03
	Al		1.32	1.49	0.83	0.08	0.08	0.10	0.09
	F		-	-	-	1.26	1.44	1.44	1.72
	Na		-	0.10	-	0.07	0.07	0.07	0.02
	P		0.07	0.07	0.12	0.22	0.22	0.28	0.20
	S		1.55	0.79	20.41	16.74	16.86	20.56	17.06
	Ti		0.08	0.07	0.03	0.02	0.02	0.01	0.02
Loss on ignition (975ºC)		*UNE-EN 1744-1:2010*	2.03	0.34	21.41	23.66	22.83	1.18	21.57

PG-D was characterised by its high contents of Ca and S: 22.5% and 16.74%, respectively. In addition, the sample contained 1.26% of F; the rest of components were in proportions less than 1%. The compositions of PG-C and PG-W were similar. However, there were slight variations in Ca and S contents in the PG-B sample. In this case, the proportions of Ca and S increased, resulting in 27.7% of Ca and 20.56% of S, although the same Ca/S relation was sustained. On the other hand, the decrease of Loss on Ignition (LOI) in PG-W was due to the loss of impurities through the washing treatment.

Table 9.1 shows that the Ca/S ratios of the PG samples were higher than those of NG. This leads us to consider that PG does not only act as a setting-time regulator in the manufacture of cement mortars; its use also improves the mortar's mechanical properties. Previous studies have shown that a high Ca/S ratio, high free lime content and high anhydrite content present in the mineral additions improves the pozzolanic activity and cementing properties [22].

Cement (Cem), Clinker (Ck) and Natural Gypsum (NG)

Portland cement clinker (Ck), made of limestone and clays heated to 1450 °C, was used to manufacture PG mortars. NG is added to the clinker in the final cement grinding process, as a set retarder, the usual levels of addition are between 3–5%. Therefore, NG was studied to compare its properties with those of PG. As shown in Table 9.1, NG is characterised by its high concentrations of Ca (23.3%) and S (20.41%). The remaining elements (Al, Fe, Mg, S and Ti) are present at less than 1%, except Si (2.98%).

Additionally, the study of cement mortars manufactured with commercial Portland cement type CEM I 42.5R was carried out. The chemical properties of this cement are shown in Table 9.1.

9.2.2 – Mix proportions

The different treated PG (PG-D, PG-C, PG-B, PG-W) were used as substitutes for NG with different percentages of addition (2.5% and 5%). Further, a control mortar was manufactured with NG (Control-NG) in this percentage a mixture of NG and PG-D (NG-PG-D 50/50) and a reference cement mortar manufactured with commercial Portland cement (Reference-Cem). The nomenclature of each manufactured cement mortar is shown in Table 9.2.

Table 9.2: Nomenclature of cement mortars

MORTAR	DESCRIPTION
Reference-Cem	Reference mortar manufactured with Cem I 42,5R
Control-NG	Reference mortar manufactured with Natural Gypsum
NG-PG-D-50/50	Mortar with Natural Gypsum and dried PG in proportions of 50%
PG-D	Mortar with dried PG
PG-B	Mortar with combusted PG
PG-C	Mortar with crushed and sieved PG
PG-W	Mortar with washed and filtered PG

The mix proportions are shown in Table 9.3. Six pieces of each specimen were manufactured. All samples were mixed by laboratory drum mixer. Then, the fresh mortar samples were placed into moulds and vibrated using a vibrating table to homogenise them. Finally, to evaluate the influence of curing characteristics of mortars, the mortars were cured in two different mediums: In a curing chamber with 50% humidity and 20 ° C of temperature and immersed in a water tank (humidity of 100% and a temperature of 20 ºC).

Table 9.3: Mortar mix proportions

		DOSAGE (g)					
		SS	**PG**	**NG**	**Cement**	**Clinker**	**Water**
Reference	Reference – Cem	1350	-	-	450	-	225
Series 1 (2.5%)	2.5Control – NG	1350	-	11.25	-	438.75	225
	2.5NG-PG-D-50/50	1350	5.625	5.625	-	438.75	225
	2.5PG-D	1350	11.25	-	-	438.75	225
	2.5PG-C	1350	11.25	-	-	438.75	225
	2.5PG-B	1350	11.25	-	-	438.75	225
	2.5PG-W	1350	11.25	-	-	438.75	225
Series 2 (5%)	5Control – NG	1350	-	22.5	-	427.5	225
	5NG-PG-D-50/50	1350	11.25	11.25	-	427.5	225
	5PG-D	1350	22.5	-	-	427.5	225
	5PG-C	1350	22.5	-	-	427.5	225
	5PG-B	1350	22.5	-	-	427.5	225
	5PG-W	1350	22.5	-	-	427.5	225

9.2.3.- Test methods

This study evaluated the cement mortars manufactured with PG as a substitute for NG according to three essential characteristics:

1) Technological tests to evaluate the mechanical behaviour and durability properties of the cement mortars. Tests of consistency,

density and setting time of fresh mortars, and flexural strength, compressive strength and shrinkage of hardened mortars were carried out.

2) A mineralogical study of the manufactured mixtures by X-ray diffraction (XRD) was performed to understand the behaviour of hardened mortars manufactured with PG. The mineralogical analysis was carried out by powder XRD analysis on a Bruker (model D8 Advance A25) with Cu anticoat. The measurement conditions were: 2? of 10-120°; step = 0.015°; t = 0.5 s; tube conditions: 40?KV and 30?mA; fixed divergence gap of 0.1°; 30 rpm spin and Ni filter. For the quantitative analysis by XRD the Rietveld method was used (TOPAZ v. 4.2 software)

3) The potential environmental impact of the manufactured mortars was studied; therefore, leaching tests were carried out on materials by the EN 12457-2 procedure. In addition to this, to evaluate the effect of PG within the cement matrix, cement mortars manufactured with 5% PG were studied according to the NF X31-211 monolithic leaching test. Before leaching, the mortars were cured for 28 days at room temperature. This test was carried out at the natural pH of the sample and the concentration of heavy metals was determined in the laboratory by inductively coupled plasma mass spectrometry (ICP-MS).

Table 9.4 shows the testing standard used.

Table 9.4: Mortar mix proportions

		Test method	Curing time
Technological tests	**Properties of fresh mortar**		
	Consistence	UNE-EN 1015-3	0 days
	Bulk density	UNE-EN 1015-6	0 days
	Setting times	UNE-EN 196-3	0 days
	Properties of hardened mortar		
	Compressive strength	UNE-EN 1015-11	1, 7, 28 days
	Flexural strength	UNE-EN 1015-11	1, 7, 28 days
	Shrinkage	UNE 83831	1, 7, 14, 28, 56 days
Mineralogical study	Powder X-ray diffraction (XRD)		28 days
Environmental feasibility	Leaching test raw material	EN 12457-2	0 days
	Monolithic Leaching tank test	NF X31-211	28 days

Statistical analysis

In order to evaluate and characterise as a whole the mechanical behaviour resulting from the use of PG in cement mortars, multivariate approaches were applied. In this context, the following parameters were used: flexural strength (FS) and compressive strength (CS). Both mechanical properties are considered as quality indicators to evaluate the potential use of different waste types in new cements [23].

Statistical data analysis included two steps: multiple linear regression (MLR) and multivariate principal component analysis (PCA). The R v.3.3.0 freeware was used to perform the statistical analyses [24]. Prior to any statistical analysis, a detailed data exploration was carried out for each PG treatment and the mechanical parameters were analysed for normality (Shapiro–Wilk test) and homogeneity of variance (Fligner test) using the package mvnomr test [25]. Log transformation was used for both CS and FS variables in order to archive normality.

MLR was applied to predict the relationships between the percentage of addition of PG and PG treatment as well as to evaluate the variation of mechanical properties over time (e.g. 7 and 28 days). It should be pointed out that the measurements of mechanical parameters at day 1 were not included because they are not significant in the mechanical behaviour of cement mortars. For each mechanical variable, two regression models were performed separately for both dry-chamber and underwater-curing conditions. Thus, the study evaluated the patterns of variability in the influence of both PG treatment and addition percentage under different curing conditions. To test them, models were analysed according to univariate analysis of variance (ANOVA) and were compared using the Chi-square test for $p \leq 0.05$. Firstly, it was necessary to choose the best-fit model, which was carried out by statistical indicators (e.g. adjusted R2 and Akaike information criterion (AIC)). In addition, the error measures of the root mean square error (RMSE) were calculated for each model developing an objective comparison of the performance of each. Finally, coefficient plots for both curing condition models were performed in order to evaluate and visualise the different patterns of influence of the variables used. MLR models were carried out by generalised linear model (GLM) methods using the Gaussian distribution family.

In a second step, principal components analysis (PCA) was carried out to analyse the mechanical behaviour of the mortars at 28 days to stablish the degree of discrimination and/or association among them. Two PCAs in particular were carried out: 1) whole-experiment design (e.g. curing treatment conditions, percentage addition of PG, and PG treatments), and 2) for each curing condition separately (e.g. dry-chamber and underwater-curing treatment conditions). A Q-mode analysis were used by the PCA through the principal functions in the psych package for carry out the breakdown of the data matrix between populations [26]. Through this analysis, a set of variables (dimensions) are created, which are the result of the linear combinations of the variables of origin. The new dimensions are independent of each other and their classification is done according to the variation shown. An orthogonal varimax gross rotation was used for the estimation of the factor loads after the initial extraction by the main method. Only factors with SS (sum of squares) loadings > 1 were extracted.

9.3.- Results and discussion

9.3.1 – Technological tests

Consistency, density and setting time

Consistency and density of cement paste were estimated before testing the setting time.

The use of PG in the manufacture of mortars resulted in consistency values lower than Reference-Cem. As the percentage of addition of PG increased, the consistency values decreased (Table 9.5). It was observed that PG provided additional stiffness to the paste, and therefore addition of water was required to obtain consistency values similar to those of the control mortars [27]. Bhadauria and Thakare, 2006 [27] showed that with 5% replacement of PG the consistency was very close to control values, being similar to the results obtained in this work (Table 9.5).

Table 9.5 shows that the PG treatment did not significantly influence the consistency values obtained. The lowest consistency values were obtained for PG-D in both series: 153 mm and 146 mm, respectively.

Unlike the consistency values, as the percentage of PG addition increased, the density values also increased (Table 5). This property was significantly influenced by the PG. Table 5 shows that mortars manufactured with crushed, burned and washed PG resulted in an increase in density with respect to mortars manufactured with PG-D. This can be attributed to the removal of impurities [28], due to the formation and hardening of the hydration products, the open pores are filled and the density increases [29].

Table 9.5: Physical properties of fresh mortars

		Consistency (mm) ***UNE-EN 1015-3***	***Density (g/cm3)*** ***UNE-EN 1015-6***	***Setting time (minutes)***	
				Initial	***Final***
Reference	Reference – Cem	166	1937	169	216
Series 1 (2.5%)	2.5Control – NG	157	2031	149	193
	2.5NG-PG-D-50/50	156	1997	163	211
	2.5PG-D	153	1974	153	209
	2.5PG-C	156	1991	132	197
	2.5PG-B	154	1982	158	213
	2.5PG-W	159	1987	146	203
Series 2 (5%)	5Control – NG	135	2028	141	187
	5NG-PG-D-50/50	152	2063	150	198
	5PG-D	146	1996	181	246
	5PG-C	149	2023	166	224
	5PG-B	148	2003	186	221
	5PG-W	153	2016	193	264

The setting times (initial and final) showed significant increases as the percentage addition of PG was increased. Similar values were obtained in previous work [30]. Setting time was always shorter for PG mortars with respect to Reference-Cem for 2.5% addition. Using more than 2.5% of PG, the setting time increased gradually; however, this was different for Control-NG and NG-PG-D 50/50. This may be due to the formation of anhydrite at an early stage [30, 31].

The processed sample PG-C with 5% addition showed optimum results for both initial and final setting time (comparable with Reference-Cem). The longer setting time was obtained for 5% PG specimens. Previous studies have shown that an increase in the amount of impurities such as fluorides [11] leads to an increase in the setting time [32–35]. Similar results are shown in Table 9.5.

Compressive and flexural strength

Figures 9.2 and 9.3 show the results for the compressive and flexural strengths of the different types of manufactured mortars. This study demonstrated that mortars cured at similar temperature and different humidity presented different technical properties. It was observed that mortars cured in underwater conditions obtained higher CS values than those cured in dry-chamber conditions for all treatments and addition percentages.

All cement mortars manufactured with PG showed higher values of CS than those manufactured with NG (Control-NG).

With respect to percentage of addition, it was generally observed that for Series 1 (2.5% addition), the processed materials showed higher CS values under both curing conditions and for all ages with respect to 2.5 PG-D, 2.5 Control-NG and 2.5 NG-PG-D 50/50 mortars. The PG treatments influenced more significantly the CS values of mortars cured in the dry chamber (Figure 9.2.B).

In Series 1 (2.5% addition), the highest values of CS were obtained for PG-W. Similar results were shown in previous studies, in which different treatments eliminated the impurities present in PG, showing that the addition of these materials in small percentages increased the CS compared to mortars manufactured with unprocessed PG [36].

As the percentage addition of PG increased, the CS also increased in underwater-cured cement mortars, due to the additional hydration of mortars, which leads to a faster pozzolanic reaction. Mortars manufactured with 5% PG obtained higher CS values than Reference-Cem and 5Control-NG cured in underwater conditions (Figure 9.2.A). Similar results were obtained by several authors, who verified that the addition of up to 10% of PG in mortars and concretes led to an increase in the values of CS [30, 37].

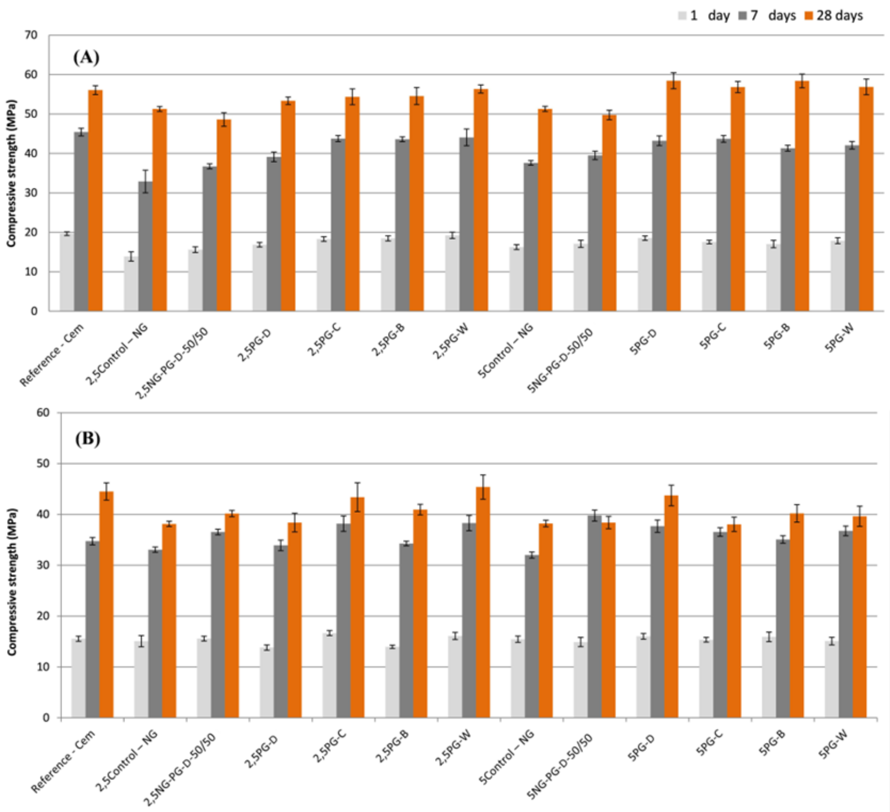

Figure 9.2: Compressive strength according to curing conditions. (A) Underwater curing condition, (B) Dry Chamber curing condition.

The increase in CS values was related to the setting time. For a 5% PG addition and underwater-curing conditions, the final setting time and the CS increased. That is, slower hydration reactions lead to higher resistances.

This showed that a greater addition of PG, due to its chemical composition, acted not only as a regulator of setting time. PG addition also provided a cementitious capacity for cement mortars similar to that provided by mineral additions, thus increasing the CS. The highest values were obtained for 5PG-D mortar (58.44 MPa), although the results for the CS of mortars manufactured with different PG treatments can be considered similar. This fact is very important since it reinforces the benefits of adding PG when making cement by reducing the amount of NG used.

Regarding FS, as the PG addition percentage increased, the FS values also increased for the two curing conditions. This increase was more significant in cement mortars cured in the dry chamber (Figure 9.3.B). this is in contrast to the CS values, where the increase in PG addition significantly increased the values for underwater-cured mortars at 28 days (Figure 9.2.A).

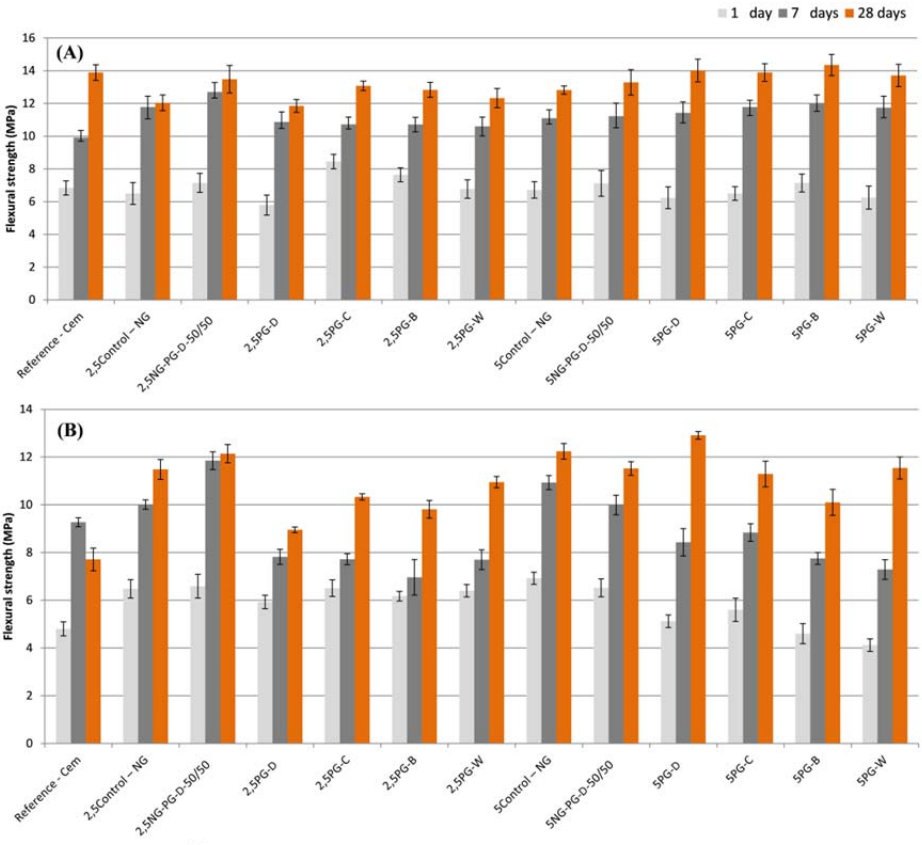

Figure 9.3: Flexural strength according to curing conditions. (A) Underwater curing condition, (B) Dry Chamber curing condition.

All mortars manufactured with 5% PG (with and without treatment) showed higher FS values than those manufactured with commercial cement OPC (Reference-OPC) for both curing conditions (Figures 9.3.A and 9.3.B).

As with the percentage of addition, the influence of PG treatment was more significant in dry-chamber-cured mortars (Figure 933.B), as the values of CS show (Figure 9.2.B).

This study showed the benefits for FS values in mortars cured in the dry chamber (Figure 9.3.B). The mortars made with PG obtained higher FS results at 28 days compared to Reference-Cem cured under these conditions.

Therefore, CS and FS values increased as the percentage of PG addition increased, obtaining higher values of these measures for underwater-cured mortars. The PG treatment was non-significant for the mechanical behaviour of mortars under these curing conditions.

Shrinkage

The dimensional instability over time of the cement mortars was studied to evaluate the influence of PG percentage addition and PG treatment on the manufacture of mortars (Figure 9.4). This figure shows that shrinkage of cement mortars with 2.5% addition of PG are very close to each other, independent of the treatment applied to PG, showing values similar to that of Reference-Cem. The mortars manufactured with NG presented greater dimensional instability than those manufactured with PG. These results have been obtained in previous studies [38], in which it was demonstrated that the higher percentage addition of NG resulted in increase in shrinkage for the cement mortars; this shrinkage increased with increasing amount of gypsum. According to the few available studies, the introduction of PG into the mortars increased shrinkage [28, 39]. In cement mortars made with 5% PG, the shrinkage values increased significantly with respect to mortars manufactured with 2.5% and Reference-Cem, as shown in Figure 9.4.

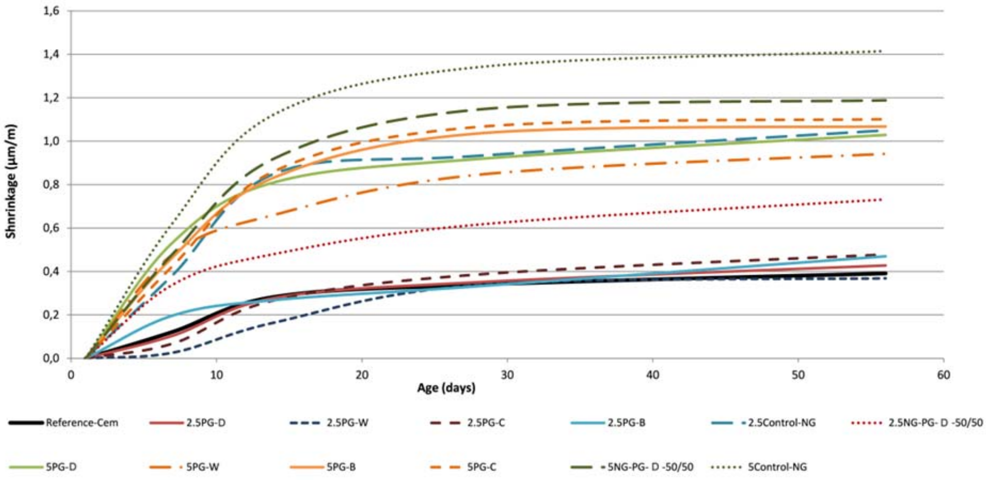

Figure 9.4: Shrinkage of the mortar as a function of age in days.

This study verified that the PG particle size does not influence the dimensional changes of the mortars, because mortars manufactured with PG-C and PG-B that have a particle size smaller than PG-D and PG-W resulted in larger dimensional changes for both series (2.5% and 5% addition). For this reason, the shrinkage in 5PG cement mortars could be due to the chemical composition of the PG material that undergoes slight changes through the application of treatments.

9.3.2 – Mineralogical study

Table 9.6 shows the result of XRD analysis of the reference, control and mortars manufactured with 5% of PG, processed and unprocessed, under different curing conditions.

Curing conditions showed variations in the mineralogical phases of cement mortars. Mortars with 5% PG cured underwater showed higher percentage of alite, belite, portlandite and ettringite. This showed that the internal reactions produced in the mortar paste took place more slowly in the presence of water, achieving greater pozzonalicity in the mixtures and an improvement in mechanical behaviour. The use of PG as an additive in cement manufacturing leads to an increase in alite (Table 9.6). The increase in alite values is related to better mechanical behaviour; alite is the primary strength-contributing phase during Portland cement hydration.

In mortars manufactured with PG, ettringite values increased and gypsum values decreased with respect to Control-NG (Table 9.6). The ettringite crystals formed at an early stage were connected to each other and built up a framework that was beneficial to early strength development [40].

Table 9.6: Structural details for phases that may be present in Series 2 of cement mortars in relation to curing conditions

Mineralogical phase (%)	Dry chamber curing					
	Reference-Cem	5Control-NG	5PG-D	5PG-C	5PG-B	5PG-W
Gypsum ($CaSO_4 \cdot 2H_2O$)	4.8	9.3	1.5	4.4	1.6	1.4
Calcite ($CaCO_3$)	7.4	11.4	11.5	10.4	10.4	13.9
Anhydrite ($CaSO_4$)	<0.1	3.1	<0.1	<0.1	<0.1	<0.1
Quartz (SiO_2)	39.5	39.8	42.5	46.5	48.7	52.6
Alite (Ca_3SiO_5)	10.4	9.2	17.7	14.3	18.9	7.2
Larnite (Belite) (Ca_2SiO_4)	13.6	11.5	3.9	7.6	1.2	10.1
Brownmillerite (Ca_2AlFeO_5)	4.1	4.2	8.2	3.7	2.6	2.4
Portlandite($CaOH_2$)	16.6	8.5	11.1	8.6	10.8	8.3
Ettringite($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$)	2.9	1.2	3.7	2.8	4.8	3.3
Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$)	<0.1	1.3	0.2	1.2	0.6	0.1

Table 9.6: Continuation

Mineralogical phase (%)	Under water curing					
	Reference-Cem	5Control-NG	5PG-D	5PG-C	5PG-B	5PG-W
Gypsum ($CaSO_4 \cdot 2H_2O$)	2.3	2.9	1.2	1.9	2.5	1.8
Calcite ($CaCO_3$)	8.9	4.6	4.6	4.7	4.3	4.2
Anhydrite ($CaSO_4$)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Quartz (SiO_2)	46.2	68.1	31.0	45.9	39.8	53.0
Alite (Ca_3SiO_5)	12.6	8.6	20.6	16.8	19.5	8.9
Larnite (Belite) (Ca_2SiO_4)	12.6	5.8	12.0	10.4	10.9	8.9
Brownmillerite (Ca_2AlFeO_5)	2.9	2.9	3.2	3.5	2.9	4.4
Portlandite($CaOH_2$)	10.8	4.7	17.2	13.2	17.2	14.1
Ettringite($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$)	2.5	1.1	5.0	2.3	1.7	3.5
Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$)	<0.1	1.1	0.7	0.9	0.9	0.6

The increase in ettringite formation was conditioned by a slower final setting time. For that reason, it was observed that mortars of Series 2 manufactured with PG, in which the setting time had been longer than the Control-NG (Table 9.5), the amount of ettringite increased (Table 9.6). The early ettringite formation acts as a layer that covers the cement grains and causes a slower setting of mortars [41]. The results showed how the presence of PG in a reacting cementitious system can influence its setting time and the crystallinity of the ettringite formed [42].

As can be seen in Table 6 on the mineralogical phase of the mortars, the curing conditions are not the only influence. The different treatments of the PG also lead to a variation of the mineralogical phases of each mortar. There was an increase in the percentage of alite and portlandite in mortars 5PG-D and 5PG-B for both curing conditions, this factor was correlated with the CS obtained at 28 days (Figure 9.2), for which it was greater in these mortars than for those using the other treatments.

The ratio plots between elements Al / Ca versus to Si / Ca were used to classify the composition of each phase [43, 44]. A previous study [45] showed that in the hydration of cements at 20 ºC, it was observed that the concentrations of Ca, N, S, Al, K and Si were related to the levels of ettringite (Ettr) and calcium monosulfate (AFm).

Figure 9.5 shows the graph generated from the Si/Ca and Al/Ca ratios obtained from the analyses performed on cement mortars that were manufactured with different 5% PG treatments. It should be noted that in the elaboration of these graphs the theoretical relationships of the involved phases were used, such as Ettr, AFm and portlandite (CH).

It can be observed in Figure 9.5 that the Si/Ca and Al/Ca ratios of mortars manufactured with PG were grouped in the area known as the C-S-H gel zone; however, it can be seen that there were significant differences between them, since both the mortars manufactured with PG-B and those manufactured with PG-W had higher Si/Ca ratios compared to those shown by the control mortars. The formation of C-S-H gel can be directly related to the setting time. The retardation in the setting for 5PG-W and 5PG-B is due to formation of silica gel or C-S-H (Table 9.5 and Figure 9.5) [46].

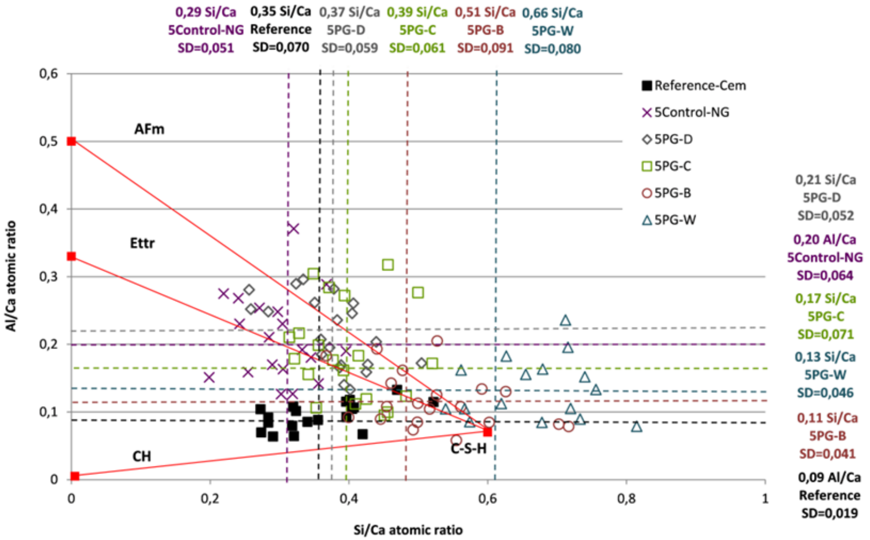

Figure 9.5: Al/Ca atomic ratio plotted against Si/Ca atomic ratio for individual X-ray microanalyses of the matrix of cement mortars at 28 days. Red points represent pure phases and red lines, a mix between two pure phases

On the other hand, it was possible to appreciate that the mortars manufactured with PG-D and PG-C showed high Al/Ca ratios. Mortars manufactured with PG-W, PG-C and PG-B were not located in the same zone; that is to say, there existed among them a very remarkable dispersion as a result of the great differences in their Si/Ca relationships, which can be associated with hydration reactions taking place very quickly.

9.3.3 – Environmental impact

One of the specific objectives of this study was to evaluate the mobility of the pollutants contained in the mortars manufactured with 5% PG in relation to Control-NG and Reference-Cem. A leaching evaluation of the PG as raw material was studied to compare the heavy-metal leach of this material into a cementitous matrix. According to Council Decision 2003/33/EC[47], a waste is classified as an inert, non-hazardous or hazardous material. Figure 9.6 shows the classification of each material.

The trace elements, Ba, Cd, As and Pb were present in the largest concentrations among all elements analysed (Figure 9.6). Previous studies have showed that PG could also boost the retention capacity of toxic elements such as As, Cd and Pb [48, 49]. However, the heavy-metal content in the by-product constitutes no environmental hazard at the rate standard established. PG is classified as a non-hazardous material because the Cd content exceeded the limits established by Council Decision 2003/33/EC [47] to be considered an inert material.

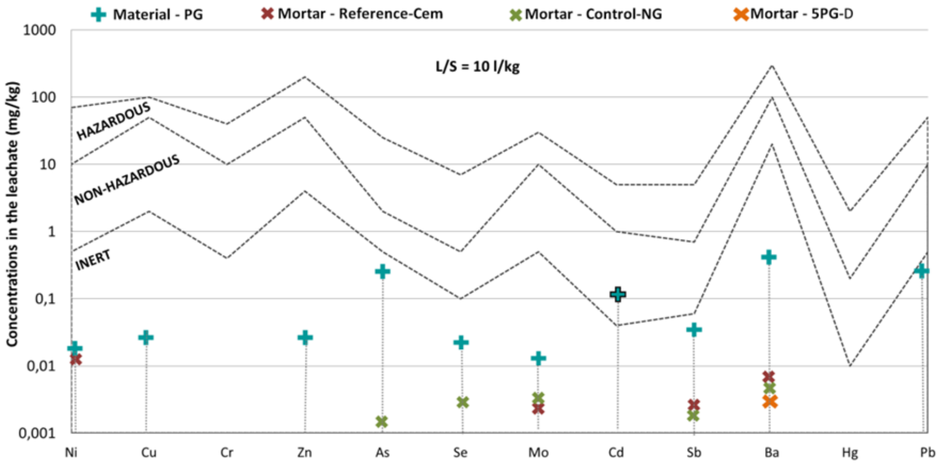

Figure 9.6: Concentrations of metals on leachate at L/S=10 L/kg and classification according to concentration on heavy metals. *Limits standard represented by dashed line.*

Figure 9.6 shows the heavy-metal leaching results of PG within a cementitious matrix. These results were compared with commercial Portland cement and a control mortar manufactured with NG. It can be seen that none of the mortars exceeded the established standard limits. Mortars manufactured with PG showed lower contents of all heavy metals except Cr and As compared to commercial Portland cement and Control-NG mortar. The results previously obtained for PG leaching according to EN 12457-2 were analysed with respect to the results obtained from PG leaching within a cementitious matrix, and a decrease in the content of heavy metals were observed in 5PG-D. Previous studies demonstrated similar results for different wastes [50].

9.3.4 – Statistical analysis

The use of a multivariate method is a suitable a waste management approach for evaluating the use of PG in cement mortars. Firstly, factors and treatments, as well as PG curing conditions, influencing the mechanical behaviour of cement mortars were determined by multiple regressions. Secondly, relationships between treatments and PG curing conditions in cement mortars were also detected by spatial discrimination with ordination analysis.

Influencing factors

A broad summary of the factors predicting the mechanical behaviour resulting from the use of PG in cement mortars is shown in Table 9.7. Overall, the variation explained by CS was larger than that by FS under both curing conditions (i.e. dry-chamber and underwater-curing conditions). In dry-chamber curing condition, variables explained 74% ($P < 0.0001$) for CS and 41% ($P < 0.0001$) for FS. And in underwater-curing condition, the same variables explained 93% ($P < 0.0001$) and 11% ($P < 0.05$) for CS and FS, respectively. This indicates that the FS of mortars is not strongly related to the treatment of the PG used, which can be observed by the homogeneity of values measured for FS, in contrast to CS (Figure 9.3). In addition, the use of different percentages of PG (AP) added to cement mortars showed dissimilar effects between FS and CS for both curing conditions, without effect for FS (Table 9.7). Similarly, this study did not detect significant changes in FS with curing time, compared to that observed for CS for both curing conditions. These findings were not surprising because it is well documented that FS has shown a low sensitivity to the use of some waste products in cement mortars [23, 51].

Table 9.7: Potential factors associated with use of different percentage and treatments of PG in cement mortars in multivariate regression analysis

	Dry chamber curing condition				Underwater curing condition			
	Compressive Strength		Flexural Strength		Compressive Strength		Flexural Strength	
	T value	*P*	T	*P*	T value	*P*	T	*P*
Intercept	52.32	***	45.62	***	64.26	***	72.7	***
Day	16.54	***	0.1	NS	43.30	***	-	NS
Percentage (AP)	1.97	*	1.27	NS	2.96	**	1.05	NS
PG treatment								
Control-NG	-2.92	**	1.59	NS	-8.33	***	-	NS
NG-PG-D-50/50	-1.39	NS	3.61	***	-7.62	***	-	NS
PG-D	-5.93	***	-2.17	*	-6.07	***	-	**
PG-C	6.66	***	-0.51	NS	-1.61	NS	-	NS
PG-B	-4.22	***	-0.88	NS	-0.29	NS	-	NS
PG-W	3.22	*	0.84	NS	-0.54	NS	-	NS
Iterations								
AP *vs* NG-PG-D-50/50	-0.72	NS	-1.14	NS	-0.36	NS	-0.62	NS
AP *vs*PG-D	2.81	**	1.69	NS	1.44	NS	1.72	NS
AP *vs*PG-C	-7.4	***	0.42	NS	-2.05	*	0.31	NS
AP *vs*PG-B	0.21	NS	-	NS	-2.87	**	1.05	NS
AP *vs*PG-W	-3.82	***	-0.91	NS	-3.22	**	0.95	NS
adjR²	**0.74**	***	**0.41**	***	**0.93**	***	**0.11**	*

*Note: *p < 0.05; **p < 0.01; ***p < 0.001; NS: No Significant*

Multiple regression analysis

For a better understanding of the behaviour of PG mortars, a more detailed study was made on the curing conditions with respect mechanical behaviour. In Figure 9.7 the variables in each sample are represented by a bar giving the 95% confidence interval of the mean results. The various samples are grouped in two groups according to CS or FS.

As expected, multiple regression analysis revealed that the use of PG treatments in cement mortars showed a stronger influence on CS than on FS (Table 9.7 and Figure 9.7). However, this dissimilar effect appeared to be mainly observed in dry-chamber curing conditions, where the most of the PG treatments showed a significant effect on CS (Table 9.7). In fact, all PG treatments, except for that based on equal combinations of unprocessed and natural gypsum treatments (NG-PG-D 50/50) showed a significant effect ($P < 0.001$) for CS in dry-chamber curing conditions. In contrast, values of CS were significantly different ($P < 0.001$) with the use of only three PG treatments, including Control-NG, NG-PG-D 50/50 and PG-D for underwater-curing conditions (Figure 9.7). One plausible explanation for this major heterogeneity is that the effect of the addition of PG on the mechanical properties of cement mortars of dry-chamber curing conditions is more significant because of the demand for water. This reduction in strength (Figures 9.2 and 9.3) may be conditioned by the absence of water in the mixture [52]. The pozzolanic effect is limited by the lack of water and leads to a reduction in the strength of PG mortars, and the results obtained were more variable.

Interestingly, the study revealed that PG-D was the most influential treatment because it exhibited values significantly different for both mechanical properties evaluated. This indicates that the use of PG as a supplementary cementing material replacing part of the clinker resulted in significant effects on CS.

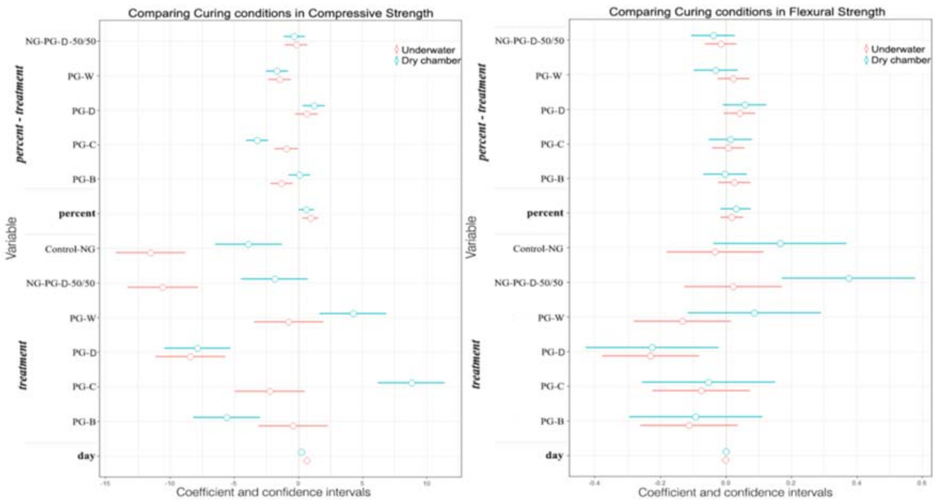

Figure 9.7: Forest plot for prognostic effect of curing conditions in mechanical behaviour for treatment efficacy, percentage of addition and day.

Principal components analysis

To analyse the degree of discrimination and/or association of the mortars by PCA, each of the samples was analysed according to different variables in relation to the mechanical behaviour. Mechanical factors were interpreted by the PCA eigenvectors.

Figure 9.8 shows the interpretation of PCA results, analysing the mechanical behaviour of hardened mortars in relation to different variables (curing conditions and percentage). Figure 9.8A shows the mortars studied in relation to the curing conditions.

The results obtained are scattered throughout Figure 9.8A but are clearly differentiated into two groups in relation to the curing conditions. According to the position of the axes of Figure 9.8A, the samples with high mechanical strengths (> CS and FS) are grouped in the right part of the figure. Underwater-cured mortars obtained higher CS and FS results.

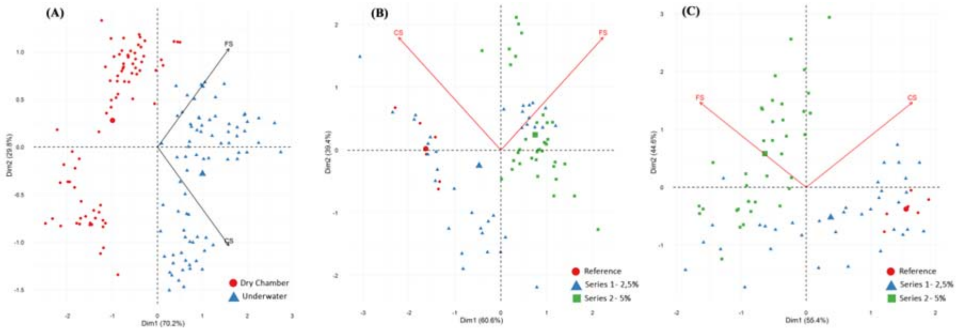

Figure 9.8: Principal Components Analysis (PCA) of mechanical parameters analyzed to evaluate the use of PG with different treatments and different percentage of addition in the manufacture of cement mortars depending to the curing conditions. (A) Curing conditions, (B) Percentage of addition in Dry Chamber Curing, (C) Percentage of addition in Underwater Curing.

For dry-chamber curing conditions, the PCA results indicate that after 28 days the FS developed by 5% PG cement mortars (Series 2) were higher in comparison to Reference-Cem and to 2.5% PG cement mortars (Series 1). The results for CS were similar for Reference-Cem and Series (Figure 9.8B). The slower hydration rate of Series 2 led to diminished strength of the hydraulic mixtures [53]. The PCA results obtained for the underwater-cured samples (Figure 9.8C) showed less dispersion than those shown in Figure 9.8B. For these curing conditions, Series 2 resulted in higher CS values than the control (Figure 9.2). This showed that a greater addition of PG with an adequate cure, due to its chemical composition provided cement mortars with a cementitious capacity similar to that provided by mineral additions, thus increasing the CS [52].

Overall, PCA demonstrated that the curing conditions in cement mortars with PG have an influence on the mechanical behaviour and produce an increase in these properties for underwater-cured mortars. On the other hand, 5% PG addition showed an improvement in the mechanical properties, despite the results being more disperse.

9.4.- Conclusions

The purpose of this paper was to investigate the consequences of different curing conditions, treatments and percentages of added phosphogypsum on the technical, mechanical and environmental properties of cement mortars. This work showed that in cement production, phosphogypsum can be used both as a setting-time regulator and as a supplementary cement material to replace natural gypsum.

Based on the results and discussion, the following conclusions were obtained:

- The high content of Ca present in PG indicates that this material can be used both as a setting regulator and as a pozzolanic addition in cement manufacture.

- The presence of anhydrite in the PG resulted in faster initial setting times in mortars manufactured with PG with respect to Reference-Cem. As the percentage of added PG increases, the setting times of mortars decrease.

- The different curing conditions significantly affected the strength of cement mortars: the curing of specimens in water resulted in higher strength values than those cured in dry chamber.

- Regarding the technological properties, the use of higher PG percentages led to an increase in alite, increasing the CS and FS in underwater-curing conditions. The internal reactions produced underwater in the mortar paste with 5% addition proceeded more slowly, achieving greater pozzolanicity in the mixtures and an improvement in mechanical behaviour. The mechanical behaviour results showed similar values for mortars made with untreated and treated PG. So, it is feasible to use PG without any type of treatment in the manufacture of cement mortars.

- Regarding environmental issues, the leaching test classified PG as a non-hazardous material. It was observed that the use of PG inside a cementious matrix reduces the emission of heavy metals; cement mortars made with PG are classified as inert.

-Finally, it was shown that MLR and PCA are useful tools to classify the mechanical properties according to the percentage of addition and treatment given to the waste for its application in the manufacture of cement mortars.

For future research, it would be interesting to use linear regression models to associate the composition of the sample with the mechanical behaviour; in this way, the evaluation of dosages and optimal treatments for the manufacture of cement mortars could be obtained.

Through the present study, the feasibility of the use of PG as a substitute for NG in the manufacture of cement mortars has been demonstrated. This by-product acts both as a setting regulator and as a mineral addition, improving the technical and mechanical properties of cement mortars.

9.5.- Standards used in the experimental work

UNE-EN 196-2:2014. Method of testing cement - Part 2: Chemical analysis of cement.

UNE-EN 1744-1:2010. Tests for chemical properties of aggregates - Part 1: Chemical analysis.

UNE-EN 1015-3:2000. Methods of test for mortar for masonry - Part 3: determination of consistence of fresh mortar (by flow table)

UNE-EN 1015-6:1999. Methods of test for mortar for masonry - Part 6: determination of bulk density of fresh mortar.

UNE-EN 196-3:2017. Methods of testing cement - Part 3: Determination of setting times and soundness.

UNE-EN 1015-11:2000. Methods of test for mortar for masonry - Part 11: determination of flexural and compressive strength of hardened mortar.

UNE 83831:2010 EX. Methods of test for hardened mortar for masonry - Determination of dimensional stability of hardened mortar for masonry.

UNE-EN 12457-2:2003. Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

NF X31-211:2012. Characterization of waste - Leaching test of a solid waste material initally massive or generated by a solidification process.

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CAPÍTULO X

CONCLUSIONES
CONCLUSIONS

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10.1.- Conclusiones

En base a los resultados obtenidos a lo largo de la investigación desarrollada y expuestos en los Capítulos 5-9 del presente documento, se establecen las siguientes conclusiones:

- **En relación a las propiedades físico-químicas de las CFB:**

    1. Las CFB presentan una distribución de tamaño de partículas continuo, característica esencial para la combinación con otros materiales en una mezcla homogénea en la elaboración de materiales en base cemento.
    2. Este subproducto se caracteriza por su baja densidad, textura rugosa y alta capacidad de absorción. Estas propiedades demuestran que la aplicación de las CFB como sustituto de materias primas naturales en materiales en base cemento dan como resultado un material con menor peso unitario (inferior a 2kg/dm^3 en hormigón). Pero a su vez, la alta capacidad de absorción puede provocar un incremento del deterioro del material.
    3. Su composición química se basa en altos contenidos de SiO_2, Al_2O_3 y CaOH. Estos valores proporcionaron reacciones puzolánicas y capacidad cementante positiva. En contraposición, los altos valores de K_2O, MgO y materia orgánica pueden condicionar el uso de este subproducto debido a que influyen negativamente en los parámetros de durabilidad.

- **En relación a las propiedades físico-químicas de las EAI:**

    1. Las EAI se caracterizan principalmente por su distribución de

tamaño de partículas continuo y de mayor tamaño que el cemento comercial y por su alto contenido en Si y Ca; esto componentes hacen que las EAI presenten propiedades para las reacciones de hidratación similares a las que presentan adiciones minerales tradicionales utilizadas en la fabricación de cemento. Por tanto, este subproducto presenta características puzolánicas.

- **En relación a las propiedades físico-químicas del FY:**

    1. El FY presenta una distribución continua del tamaño de partículas. Desde el punto de vista morfológico, el tamaño de partículas varía entre 0.250 y 0.045 mm. La finura del material afecta directamente a las propiedades mecánicas de los morteros de cemento fabricados con este subproducto.
    2. Relativo a las propiedades químicas, El FY presenta altos contenido en Ca y S. El alto contenido de Ca presente indica que este material se puede usar en conjunto como regulador de fraguado y como adición puzolánica en la fabricación de cemento. Las altas relaciones de Ca/S comparándolas con las que posee el yeso natural llevan a considerar que el FY presenta características cementantes.

- **En relación a la influencia de aplicación de tratamientos en la modificación de las propiedades de los subproductos industriales:**

    1. El procesamiento de los tres subproductos industriales mediante tratamientos sencillos lleva a una modificación en las propiedades físicas y químicas del material, estas modificaciones resultan en una mejora de las propiedades técnicas de los materiales en base cemento fabricados.
    2. Tratamientos sencillos de calcinación, trituración o eliminación de partículas ligeras en las **CFB** lleva a una reducción del contenido de materia orgánica. La combinación de los tres tratamientos reduce el contenido de materia orgánica de 4.34% a 0.98%. Estando

directamente relacionado con un mejor comportamiento mecánico en los morteros de cemento. Además, la utilización de CFB procesadas lleva a una disminución de la porosidad del material, propiedad relacionada con los cambios dimensionales producidos en los morteros de cemento.

3. El contenido de SiO_2 y CaOH aumenta en las muestras de CFB procesadas, viéndose directamente relacionado con el comportamiento mecánico de los morteros de cemento, aumentando la resistencia a compresión en morteros fabricados con CFB que poseen altos contenidos de ambos componentes, debido a que se causan reacciones puzolánicas produciendo una capacidad cementante positiva.

4. De forma similar se pudo observar en las propiedades adquiridas por las **EAI** después de ser sometidas a tratamientos de calcinación y trituración. La porosidad del material disminuyó considerablemente cuando fue sometido a este procesamiento combinado. Todos los morteros fabricados con EAI procesadas mostraron mejor comportamiento mecánico que los fabricados con EAI sin procesar. Los valores más altos de resistencia a compresión se obtuvieron en morteros fabricados con EAI triturada y calcinada, mostrando valores que superaron al mortero de control para 10% de sustitución.

5. La influencia de aplicar diferentes procesamientos a las CFB y EAI para mejorar las propiedades de los materiales en base cemento fabricados con estos subproductos no se observó en el estudio realizado con FY.

6. El FY fue procesado mediante trituración, calcinación y lavado. La composición química del material únicamente se vio alterada cuando fue calcinado, mostrando valores más altos de Ca y S. Traduciéndose este incremento en un retraso en el tiempo de fraguado de los morteros de cemento. Respecto a las propiedades mecánicas, el FY procesado no mostró valores significativamente variables a los obtenidos con la aplicación de FY sin procesar.

- **En relación a la viabilidad de uso de CFB en materiales en base cemento:**

1. El uso de CFB en combinación con ARM en la fabricación de **hormigón ligero** dio como resultado hormigones con densidades inferiores a 2 kg/dm^3. Las propiedades principales que presentan los hormigones ligeros fabricados con CFB y ARM son una baja densidad y alta porosidad.
2. La incorporación de CFB y ARM provoca una disminución de la resistencia a compresión en relación a la obtenida por el hormigón ligero de referencia (CONTROL). Evaluando las tasas de sustitución, las menores pérdidas de resistencia a compresión se obtienen para el reemplazo de las diferentes fracciones de áridos naturales por el 50% de ARM y el 30% de CFB y por el 75% de ARM y 15% de CFB, suponiendo una disminución entre el 14-15%.
3. A pesar de esta reducción de la resistencia a la compresión, todos los hormigones ligeros fabricado con CFB y ARM están dentro de los límites establecidos por la EHE para hormigón ligero estructural y no estructural (valor mínimo 15-20 MPa). Por lo que se demuestra que el uso combinado de ARM y CFB como sustituto de áridos naturales en la fabricación de hormigón ligero da como resultado un material de reducida densidad y características técnicas que cumplen con los requisitos mínimos establecidos.
4. Respecto al uso de CFB como sustitutivo de cemento y/o cal en la **estabilización de suelos expansivos**, las variaciones volumétricas (expansión o hinchamiento) es la propiedad con mayor incidencia, logrando una reducción del 99.5 con la adicción de un 50% de CFB.
5. Mediante la estabilización con CFB, un suelo arcilloso calificable como marginal, puede convertirse en tolerable o adecuado, permitiendo su utilización en cualquier zona del terraplén, aunque el PG3, descarta los suelos inadecuados y los marginales para la formación de terraplenes, pero establece que los suelos marginales bajo determinadas circunstancias y estudios adicionales se podrían utilizar para tal finalidad.
6. Además, las cenizas de biomasa presentan un bajo contenido en

azufre, lo que impide la formación de fases expansivas en el suelo estabilizado, como es el caso de la etringita, por lo que se resuelve de este modo los problemas a largo plazo que presenta la estabilización con cal al encontrarse azufre en la composición.

7. Además, la adición de CFB, proporciona sílice y alúmina necesaria para producir las reacciones puzolánicas que cementan la mezcla. Con esto, es posible consolidar estructuras estables y resistentes como se muestra en el estudio de la capacidad de soporte y la resistencia efectiva donde aumenta el ángulo de fricción, que es de 41 °.
8. El uso de CFB como material estabilizador de suelo resulta en una mejora considerable en terrenos expansivos similares a las conseguidas mediante la estabilización con cemento, por lo que su uso se considera viable.
9. Por último, tras el análisis de las propiedades cementantes que presentan las CFB se evalúa su uso como sustituto de cemento en la fabricación de **<u>morteros de cemento</u>**.
10. La densidad de los morteros de cemento disminuye a medida que aumenta el porcentaje de BBA como sustituto del cemento. El uso de BBA condujo a una mayor porosidad del material que produjo un aumento en la absorción de agua, estando este factor directamente relacionado con los cambios dimensionales producidos en los morteros. El uso de BBA con tratamientos de calcinación, trituración y eliminación de partículas ligeras da como resultado morteros con menor porosidad y cambios dimensionales más pequeños para una sustitución del 20% del cemento, obteniendo valores similares a los presentados por un mortero de Control.
11. El uso de CFB en la fabricación de morteros de cemento produce una disminución de los valores de resistencia a compresión. Sin embargo, en morteros de cemento con una relación de reemplazo del 20%, esta pérdida de resistencia a compresión se reduce. Los morteros de cemento con BBA triturada, calcinada y sin flotantes (proceso que lleva a una reducción del contenido de materia

orgánica y a un incremento de la presencia de SiO_2 y CaOH) mostraron un 10% de pérdida de resistencia a compresión con respecto a la mezcla de Control.

12. Aplicando procesos de combustión y trituración, se logra un aumento del 80% en la resistencia a compresión y flexión de los morteros para un 20% de sustitución respecto a morteros fabricados con CFB no procesadas y se observó un aumento del 100% en estas propiedades con sustituciones del 38.5%.
13. Por lo tanto, se demuestra que la aplicación de CFB procesado como un sustituto del cemento en la producción de morteros es factible mediante tratamientos de trituración y combustión llegando a porcentajes de sustitución de hasta el 20%, obteniéndose valores de 44.17 MPa, próximos a los exigidos para un Cem I (52.5MPa). Además, se puede aplicar un tratamiento de eliminación de partículas ligeras que incrementa la resistencia a compresión hasta valores de 51.96 MPa, pero es un proceso costoso y difícil.

- **En relación a la viabilidad de uso de EAI en materiales en base cemento:**

1. El uso de EAI en la fabricación de **morteros de cemento** da lugar a un incremento de la porosidad del material a medida que el porcentaje de sustitución aumenta. Para el 10% de sustitución, estos valores fueron similares al Control. Los tratamientos de calcinación y trituración de las EAI, disminuyen la presencia de poros en los morteros de cemento, reduciendo la absorción de agua y en consecuencia, los cambios dimensionales como contracción que se producen durante el proceso de hidratación y fraguado.
2. Los resultados más significativos que muestra el estudio de EAI como sustituto de cemento es que para porcentajes de 10%, la resistencia a compresión aumenta un 8.5 % respecto a un mortero de Control, alcanzando los 61.87 MPa en morteros fabricados con escorias trituradas y calcinadas. A medida que el porcentaje de

sustitución aumenta, la resistencia a compresión y flexión disminuye. A pesar de esta disminución, el reemplazo del 20% de cemento por EAI procesada está dentro de los mínimos establecidos para la fabricación de un Cem I (52,5MPa).

3. A pesar de que el aumento de EAI supone un empeoramiento mecánico de los morteros de cemento es necesario evaluar el uso eficiente del material aglutinante (cemento) mediante un indicador de intensidad (bi) que evalúa el consumo de aglutinante en relación a las propiedades técnicas. Los mejores índices se obtuvieron para los morteros S30-Sw-CB resultando en buenas propiedades técnicas en relación a la cantidad de cemento utilizado. Un poco menos favorable fue el uso de Sw-CB para la serie 2. Los resultados menos satisfactorios se obtuvieron con una mayor cantidad de cemento en el caso de la serie 1 con un 10% de reemplazo.
4. En comparación con la fabricación de morteros de cemento con cenizas volantes convencionales en los mismos ratios de sustitución, todos los morteros fabricados con EAI resultaron en un mejor comportamiento mecánico.
5. Mediante la aplicación de un análisis multivariante se clasifican las EAI según su durabilidad, comportamiento mecánico, tratamiento y tasa de reemplazo. En general, este análisis muestra que las tasas de reemplazo superiores al 20% de EAI en los morteros fabricados no producen ninguna mejora en las propiedades mecánicas y de durabilidad, excepto cuando las EAI son trituradas y quemadas (S30-Sw-CB).
6. En conclusión, reemplazar el cemento con EAI para la fabricación de mortero mejora las propiedades mecánicas hasta cierto grado de sustitución. Es recomendable reemplazar hasta 20% de cemento con EAI triturado, obteniéndose valores similares al Control. Por otro lado, para la sustitución de más del 20%, es necesario un proceso combinado de trituración y calcinación.

- **En relación a la viabilidad de uso de FY en materiales en base cemento:**

1. El uso de FY como **sustituto del yeso natural en la fabricación de cemento** lleva a un retraso del tiempo de fraguado a medida que el porcentaje de adición de este residuo aumenta.
2. Morteros de cemento con adición del 5% de FY muestran mayor porcentaje de alita, belita, portlandita y ettringita. El aumento de los valores de alita se relacionan con un mejor comportamiento mecánico. Debido a la presencia de alita en la fase de contribución de la resistencia primaria durante la hidratación del cemento Portland. El aumento en la formación de ettringita fue condicionado por un tiempo de fraguado final más lento. Debido a la presencia de estos elementos las reacciones internas producidas en la pasta de mortero se realizan más lentamente con la presencia de agua, logrando una mayor puzonalidad en las mezclas y una mejora en el comportamiento mecánico.
3. Mayor porcentaje de adición de FY en la fabricación de morteros de cemento lleva a un aumento de los valores de resistencia a compresión. Esto demuestra que debido a su composición química, el PG no solo actúa como un regulador del tiempo de fraguado. La adición de PG también proporciona capacidad cementante para los morteros de cemento similar a la proporcionada por las adiciones de minerales, aumentando así la resistencia a la compresión.
4. Mediante un análisis de regresión múltiple se observa la influencia de las condiciones de curado en el comportamiento mecánico. El tratamiento de calcinación, trituración y lavado del FY no tiene efecto significativo bajo condiciones de curado sumergido, siendo el FY sin ningún tipo de tratamiento el que muestra resultados más relevantes en relación al comportamiento mecánico. A diferencia del porcentaje de adición de FY que si muestra efecto significante para todos los tratamientos.
5. El análisis de ordenación revela una fuerte influencia de las condiciones de curado en las propiedades mecánicas con un efecto

de disgregación de los tratamientos aplicados al FY bajo condiciones de curado en cámara seca, sin embargo en curado sumergido no se observa disgregación como muestra el método de regresión. En general, el análisis de ordenación demuestra que las condiciones de curado en morteros de cemento con FY influyen en el comportamiento mecánico y producen un aumento en estas propiedades para el curado de morteros bajo el agua. Por otro lado, el 5% de la adición de FY muestra una mejora en las propiedades mecánicas.

6. A través del presente estudio, se ha demostrado la viabilidad de uso de FY como sustituto de yeso natural en la fabricación de morteros de cemento. Este subproducto actúa como regulador de fraguado y como adición mineral, mejorando las propiedades técnicas y mecánicas de los morteros de cemento.

En relación al impacto ambiental causado por lixiviación.

1. Los datos de la prueba de cumplimiento muestran valores que exceden de los límites para establecer el material granular como inerte. Las CFB presentan altos contenidos en Hg. Las EAI muestran altos contenidos en Cr y Mo y el FY alto contenido en Cd. Los tres subproductos son clasificados como no peligrosos.
2. El estudio particular realizado de la cantidad de Cr presente en las EAI debido a que la normativa limita la presencia de Cr VI soluble en agua en el cemento demuestra que este elemento no aparece como Cr VI, por lo que la aplicación de esta escoria en la producción de cemento es posible sin exceder los límites exigidos por la ley.
3. El uso de FY dentro de una matriz cementante reduce la emisión de metales pesados; Los morteros de cemento hechos con FY se clasifican como inertes.

Por consiguiente, y basándonos en la investigación desarrollada en la presente Tesis Doctoral las conclusiones generales obtenidas son las siguientes:

Los áridos reciclados mixtos, cenizas de fondo de biomasa, escorias de acero inoxidable y fosfoyeso se consideran subproductos industriales con elevado potencial para ser reutilizado en la fabricación de materiales en base cemento, consiguiendo de esta forma introducirlos como nuevos recursos en el proceso de producción para avanzar hacia la consolidación de economía circular.

El estudio de estos subproductos ha demostrado su viabilidad de uso como sustituto de áridos naturales, cemento y yeso natural en diferentes materiales de construcción en base cemento y como estabilizador de suelos expansivos; demostrando a lo largo de la investigación desarrollada las características puzolánicas que poseen dichos materiales. La utilización de estos subproductos contribuye a una construcción sostenible, mejorando en ciertas medias las propiedades de los elementos constructivos tradicionales. Consiguiéndose mediante su aplicación una reducción del consumo de recursos naturales, reducción de la acumulación en vertedero con el impacto ambiental que esto conlleva y un material resultante de mejores características técnicas.

10.2.- Conclusions

Based on the results obtained throughout the research developed and explained in Chapters 5-9 of this document, the following conclusions are obtained:

- **In relation to the physical-chemical properties of the BBA:**
  1. BBA shows continuous particle size distribution; this is an essential feature for the best combination with other materials in a homogeneous mixture for the production of cement-based materials.
  2. This by-product is characterized by its low density, rough texture and high absorption capacity. These properties show that the application of BBA as a substitute for natural raw materials in cement-based materials results in a material with a lower unit weight (less than 2kg / dm^3 in concrete). But at the same time, the high absorption capacity can cause an increase in the deterioration of the material.
  3. Its chemical composition shows high contents of SiO_2, Al_2O_3 and CaOH. These values provided pozzolanic reactions and positive cementing capacity. In contrast, the high values of K_2O, MgO and organic matter can condition the use of this by-product because they negatively influence in durability properties.

- **In relation to the physical-chemical properties of the SW:**
  1. SW is characterized mainly by their continuous particle size distribution. These particles show a larger size respect to the commercial cement particle size. SW are also characterized by their high content of Si and Ca; these components favour that SW show positive properties for hydration reactions similar to those that present traditional mineral additions used in the manufacture of cement. Therefore, this waste has pozzolanic characteristics.

- **In relation to the physical-chemical properties of PG:**
    1. PG shows a continuous particle size distribution. From the morphological point of view, the particle size ranges between 0.250 and 0.045 mm. The fineness of the material directly affects the mechanical properties of cement mortars manufactured with this waste.
    2. Regarding the chemical properties, PG shows high content in Ca and S. The high content of Ca leads to the fact that this material can be used both as a setting regulator and as well as a pozzolanic addition in the manufacture of cement. The high Ca / S ratios compared to those of natural gypsum lead to consider that the PG shows cementing characteristics.

- **In relation to the influence of the application of treatments on the modification of the properties of industrial waste:**
    1. The processing of the three industrial waste through simple treatments leads to a modification in the physical and chemical properties of the material, these modifications result in an improvement of the technical properties of the cement-based materials manufactured.
    2. Simple treatments of burning, crushing or removing lightweight particles in **BBA** lead to a decrease in the organic matter content. The blends of the three treatments decrease the organic matter content from 4.34% to 0.98%. This fact is directly related to a better mechanical behaviour in cement mortars. In addition, the use of processed BBA leads to a decrease in the porosity of the material, property directly related to the dimensional changes produced in cement mortars. These dimensional changes are lower in cement mortars manufactured with BBA processed.
    3. SiO_2 and CaOH content increase in the processed BBA samples, being directly related to the mechanical behaviour of cement

mortars. Mortars manufactured with BBA which show both elements increased the compressive strength, because they are caused pozzolanic reactions producing a positive cementing capacity.

4. Similarly it was observed in the properties acquired by the **SW** after being subjected to burning and crushing treatments. The porosity of the material decreases considerably when it is subjected to this combined processing. All mortars manufactured with SW processed show better mechanical behaviour than those made with unprocessed SW. The highest values of compressive strength are obtained in mortars manufactured with crushed and burned SW, showing values that exceeded the control mortar for 10% substitution of SW.

5. The influence of applying different processes to the BBA and SW to improve the properties of cement-based materials made with these by-products is not observed in the study carried out with PG.

6. PG is processed by crushing, calcination and washing. The chemical composition of the material is only altered when it is burned, showing higher values of Ca and S. The increase in the content of these elements led to a delay in the setting time of the cement mortars. Regarding the mechanical properties, mortars with processed PG not show significantly variable values to those obtained with the application of unprocessed PG.

- **In relation to the feasibility of using CFB in cement-based materials:**

1. The use of BBA in combination with RMA in the manufacture of **lightweight concrete** results in concretes with densities below 2 kg/dm^3. The main properties of lightweight concrete manufactured with BBA and RMA are low density and high porosity.

2. The incorporation of BBA and RMA cause a decrease in compressive strength in relation to that obtained by reference lightweight concrete (CONTROL). Evaluating substitution rates, the lowest compressive strength losses are obtained for the replacement of the different

fractions of natural aggregates by 50% of RMA and 30% of BBA and by 75% of RMA and 15% of BBA, assuming a decrease between 14-15%.

3. Despite this reduction in compressive strength, all lightweight concretes manufactured with BBA and RMA are within the limits established by the EHE for structural and non-structural lightweight concrete (minimum value 15-20 MPa). Therefore, it is demonstrated that the combined use of RMA and BBA as a substitute for natural aggregates in the manufacture of lightweight concrete results in a material of reduced density and technical characteristics that meet the minimum requirements established.
4. Regarding the use of BBA as a substitute for cement and / or lime in the **stabilization of expansive soils**, the volumetric variations (expansion or swelling) is the property with the highest incidence, achieving a reduction of 99.5 with the addition of 50% of BBA.
5. By stabilizing with BBA, a clayey soil qualifying as marginal can become tolerable or adequate, allowing its use in any area of the embankment.
6. In addition, the biomass ash presented a low sulfur content, which prevents the formation of expansive phases in the stabilized soil, as is the case of ettringite. In this way, the long-term problems presented by the stabilization with lime when sulfur is present in the composition are solved.
7. Also, the addition of BBA, provide silica and alumina necessary to produce the pozzolanic reactions that cement the mixture. With this, it is possible to consolidate stable and resistant structures as shown in the study of bearing capacity and effective resistance where the angle of friction increases, being 41°.
8. The use of BBA as soil stabilizer material results in a considerable improvement in expansive soils similar to those achieved through stabilization with cement, so its use is considered feasibility.
9. Finally, after the analysis of the cementing properties presented by the BBA, its use as a substitute for cement in the manufacture of **cement mortars** is analyzed.

10. The density of cement mortars decreases as the percentage of BBA increases as a substitute for cement. The use of BBA led to a greater porosity of the material that produced an increase in the absorption of water, this factor being directly related to the dimensional changes produced in the mortars. The use of BBA with calcination, crushing and elimination of light particles treatments results in mortars with lower porosity and smaller dimensional changes for a 20% substitution of cement, obtaining values similar to those presented by a Control mortar.

11. The use of BBA in the manufacture of cement mortars shows a decrease in the values of compressive strength. However, in cement mortars with a 20% replacement ratio, this loss of compressive strength is reduced. Cement mortars with crushed, calcined and without light particles BBA (a process that leads to a reduction in the content of organic matter and an increase in the presence of SiO_2 and CaOH) show a 10% loss of compressive strength with respect to Control mixture.

12. Through the application of combustion and crushing processes, an 80% increase in the compressive and flexural strength of the mortars is achieved for a 20% substitution respect to mortars made with unprocessed BBA. A 100% increase is observed in these properties with substitutions of 38.5%.

13. Therefore, it is demonstrated that the application of processed BBA as a substitute for cement in the production of mortars is feasible through crushing and combustion treatments for 20% substitution percentage, obtaining values of 44.17 MPa, close to the required for a Cem I (52.5MPa). In addition, a light particle removal treatment increases the compressive strength up to values of 51.96 MPa, but it is a costly and difficult process.

- **In relation to the feasibility use of SW in cement-based materials:**

1. The use of SW in the manufacture of **cement mortars** results in an increase in the porosity of the material as the percentage of

substitution increases. For 10% substitution, these values were similar to the Control. The calcination and crushing treatments of the SW decrease the presence of pores in the cement mortars, reducing the absorption of water and consequently, the dimensional changes such as contraction that occur during the hydration and setting process.

2. The most significant results shown by the study of SW as a substitute for cement is that for percentages of 10% the compression resistance increases by 8.5% respect to a Control mortar, reaching 61.87 MPa in mortars made with crushed and calcined slag. As the percentage of substitution increases, the compressive and flexural strength decreases. Despite this decrease, the replacement of 20% of cement by SW processed is within the minimum established for the manufacture of a Cem I (52.5MPa).

3. Although the SW increase implies a mechanical worsening of the cement mortars, it is necessary to evaluate the efficient use of the binder material (cement) by means of an intensity indicator (bi) that evaluates the consumption of cement in relation to the technical properties. The best indices were obtained for the S30-Sw-CB mortars, resulting in good technical properties in relation to the amount of cement used.

4. Mortars manufactured with SW show a better mechanical behaviour in comparison with cement mortars with conventional fly ash in the same substitution ratios.

5. Through the application of a multivariate analysis, the SW are classified according to their durability, mechanical behaviour, treatment and replacement rate. In general, this analysis shows that replacement rates of more than 20% SW in manufactured mortars do not produce any improvement in mechanical properties and durability, except when the SW are crushed and burned (S30-Sw-CB).

6. In conclusion, replacing cement with SW for the manufacture of cement mortars improves the mechanical properties to a certain degree of substitution. It is advisable to replace up to 20% cement with crushed SW, obtaining similar values to the Control. On the other hand, for the substitution of more than 20%, a combined crushing and

calcination process is necessary.

- **In relation to the feasibility use of PG in cement-based materials:**

1. The use of PG as a **substitute for natural gypsum in the manufacture of cement** leads to a delay in the setting time as the percentage of addition of this waste increases.
2. Cement mortars with 5% PG addition show higher percentage of alite, belite, portlandite and ettringite. The increase in alite values is related to a better mechanical behaviour. Due to the presence of alite in the contribution phase of the primary resistance during the hydration of Portland cement. The increase in ettringite formation was conditioned by a slower setting time. Due to the presence of these elements the internal reactions produced in the mortar paste are carried out more slowly with the presence of water, achieving a greater puzonality in the mixtures and an improvement in the mechanical behaviour.
3. Greater percentage of PG addition in the manufacture of cement mortars leads to an increase in the values of compressive strength. This shows that due to its chemical composition, the PG not only acts as a regulator of the setting time. The addition of PG also provides cementitious capacity for cement mortars similar to that provided by the traditional mineral additions, thus increasing the compressive strength.
4. Through a multiple regression analysis, the influence of the curing conditions on the mechanical behaviour is observed. The treatment of calcination, crushing and washing of PG has no significant effect in underwater curing conditions. PG without any type of treatment shows the most relevant results in relation to mechanical behaviour. Unlike the percentage of addition of PG which shows a significant effect for all treatments.
5. The principal components analysis reveals a strong influence of the curing conditions on the mechanical properties with a scattering effect of the treatments applied to the PG under dry-chamber curing conditions. However in underwater curing no disperse is observed as

shown by the method of regression. Overall, principal components analysis demonstrates that the curing conditions in cement mortars with PG influence on the mechanical behaviour and produce an increase in these properties for mortars underwater curing. On the other hand 5 % of PG addition shows an improvement in the mechanical properties despite of the results were more disperses.

- **In relation to the environmental impact caused by leaching.**

1. The compliance test data shows values that exceed the limits to establish the granular material as inert. BBA show high contents in Hg. SW show high contents in Cr and Mo and PG high content in Cd. The three by-products are classified as non-hazardous.
2. Because the regulation limits the presence of water-soluble Cr VI in the cement. The particular study performed on the amount of Cr present in SW shows that this element does not appear as Cr VI, so the application of this slag in the Cement production is possible without exceeding the limits required by law.
3. The use of PG within a cementing matrix reduces the emission of heavy metals; Cement mortars made with PG are classified as inert.

Therefore, and based on the research developed in this Doctoral Thesis, the general conclusions obtained are the following:

Mixed recycled aggregates, biomass bottom ash, stainless steel slag and phosphogypsum are considered industrial by-products with high potential to be reused in the manufacture of cement-based materials, thus getting them as new resources in the production process for move towards the consolidation of the circular economy.

The study of these by-products has proven its feasibility as a substitute for natural aggregates, cement and natural gypsum in different cement-based construction materials and as a stabilizer for expansive soils; demonstrating throughout the developed research the pozzolanic characteristics that these materials possess. The use of these by-products contributes to a sustainable construction, improving in certain means the properties of the traditional constructive elements. Through its application, a reduction in the consumption of natural resources, reduction of landfill accumulation with the environmental impact that this entails and a material resulting from better technical characteristics are achieved.

10.3.- Futuras líneas de investigación

Este trabajo deja abierta algunas líneas de investigación que podrían ser abordadas en el futuro partiendo de los resultados obtenidos. Como ampliación de los estudios desarrollados en la presente Tesis Doctoral, se sugieren las siguientes líneas de investigación:

En primer lugar, las características de las Cenizas de Fondo de Biomasa mostradas en esta Tesis, lleva a considerar importante el estudio de las propiedades de aislamiento térmico, acústico, resistencia al fuego y durabilidad de hormigones ligeros fabricados con este residuo. De esta forma, se desarrollaría un estudio de dosificaciones óptimas que redujeran drásticamente la cantidad de cemento y arena natural utilizados y diera como resultado un material de bajo peso unitario con alta capacidad aislante. Consiguiendo un material sostenible y eficientemente energético.

Por otro lado, los resultados positivos obtenidos en los estudios de aplicación de Escorias de Acero Inoxidable llevan a profundizar en la investigación de este residuo. En primer lugar, sería interesante la evaluación de la presencia de cromo en esta escoria, evaluando si la aparición es como cromo III o cromo VI, así como, la activación de este metal mediante diferentes tratamientos aplicados a las escorias y cómo evoluciona la presencia del mismo sometiendo a materiales en base cemento fabricados con escorias de acero inoxidable a procesos de oxidación y carbonatación.

Una vez evaluadas las propiedades ambientales mediante el estudio del cromo sería interesante el estudio combinado de escorias de acero inoxidable y fosfoyeso en la fabricación de hormigones autocompactantes. Suponiendo un desafío la preparación de una mezcla hidráulica con una reología adecuada mediante la aplicación de fosfoyeso como adición y regulador de la consistencia y la utilización de escorias de acero inoxidable como un potenciador de las propiedades mecánicas.