
DESARROLLO DE MATERIALES DE CONSTRUCCIÓN
SOSTENIBLES BASADOS EN CEMENTANTES DE ÓXIDO DE
MAGNESIO DE BAJO IMPACTO AMBIENTAL. APLICACIÓN A LA
ESTABILIZACIÓN DE SUELOS CON SULFATOS

TESIS DOCTORAL

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A		<i>M-S-H: Silicatos de magnesio hidratados</i>	16, 26
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G		S	
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TESIS POR COMPENDIO DE PUBLICACIONES

La presente tesis doctoral es un compendio de publicaciones científicas y se ha realizado según las especificaciones del "Acuerdo A3/2015 del Comité de Dirección de la Escuela de Doctorado de Navarra adoptado en sesión celebrada el 11 de febrero de 2015 por el que se modifica la normativa para la elaboración de tesis como compendio de publicaciones".

Las publicaciones incluidas en la presente tesis son:

- **ARTÍCULO 1:** Seco, A., del Castillo, J. M., Espuelas, S., Marcelino, S., & Echeverría, A. M. (2022). Assessment of the ability of MgO based binary binders for the substitution of Portland cement for mortars manufacturing. *Construction and Building Materials*, 341, 127777.
<https://doi.org/10.1016/j.conbuildmat.2022.127777>
- **ARTÍCULO 2:** Seco, A., del Castillo, J. M., Perlot, C., Marcelino, S., & Espuelas, S. (2022). Recycled granulates manufacturing from spent refractory wastes and magnesium based binder. *Construction and Building Materials*, 365, 130087.
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- **ARTÍCULO 3:** Seco, A., del Castillo, J. M., Espuelas, S., Marcelino-Sádaba, S., & García, B. (2021). Stabilization of a Clay Soil Using Cementing Material from Spent Refractories and Ground-Granulated Blast Furnace Slag. *Sustainability*, 13 (6), 1-16.
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- **ARTÍCULO 4:** Seco, A., del Castillo, J. M., Espuelas, S., Marcelino, S., & García, B. (2020). Sulphate soil stabilisation with magnesium binders for road subgrade construction. *International Journal of Pavement Engineering*, 23 (6) 1-11.
<https://doi.org/10.1080/10298436.2020.1825711>
- **ARTÍCULO 5:** Seco, A., del Castillo, J. M., Perlot, C., Marcelino-Sádaba, S., Prieto, E., & Espuelas, S. (2022). Experimental Study of the Valorization of Sulfate Soils for Use as Construction Material. *Sustainability*, 14(11), 6609.
<https://doi.org/10.3390/su14116609>

RESUMEN

La presente tesis por compendio de publicaciones recoge la investigación realizada para la estabilización de suelos con sulfatos, dentro del contexto de la ingeniería civil, mediante el empleo de cementantes hidráulicos basados en el óxido de magnesio (MgO). Para ello se han desarrollado y ampliado investigaciones previas relacionadas con el uso de un cemento basado en la activación de escoria granulada de alto horno (GGBS: Ground Granulated Blast-furnace Slag) mediante la adición de un MgO de bajo grado de pureza. El MgO empleado en esta investigación procede de residuos o subproductos generados en los procesos de fabricación y uso de material refractario manufacturado a partir de la calcinación del mineral magnesita. La investigación llevada a cabo parte de otras investigaciones previas que derivaron en el desarrollo del citado cementante patentado de forma conjunta por la empresa Magnesitas Navarra S.A. (MAGNA) y la Universidad Pública de Navarra (patente conjunta UPNA/MAGNA "Ligante hidráulico para materiales de construcción"). Este producto presentó una potencialidad muy alta para su empleo en la estabilización de suelos, así como una baja reactividad con los sulfatos, pudiendo limitar los efectos adversos que se producen en la interacción entre los sulfatos y los aditivos estabilizantes basados en el óxido de calcio (CaO) como son los cementos comunes y la cal (únicos estabilizantes indicados en la normativa nacional para la construcción de carreteras), lo que deriva en la generación de sulfatoaluminatos hidratados del grupo de la etringita, de muy alta capacidad expansiva.

En esta investigación se han analizado aplicaciones de cementantes hidráulicos basados en el empleo de diferentes productos y subproductos ricos en magnesio; trasladando posteriormente el conocimiento adquirido a su aplicación como estabilizadores de suelos con alto contenido en sulfatos. Para ello se construyó y estudió una zona de pruebas de campo. Así, la investigación se ha desarrollado en dos bloques o fases globales:

- Una primera donde se han caracterizado cementantes basados en la activación del GGBS con productos, subproductos y residuos ricos en MgO; valorando las características físicas que estos pueden desarrollar en la producción de morteros y agregados artificiales (gránulos), comparando estos resultados con los obtenidos en otros morteros y gránulos fabricados con un cemento común. Esta fase de la investigación derivó en la publicación de los artículos nº 1 y 2.
- La segunda fase de investigación, se desarrolló mediante la aplicación de cementantes basados en MgO para la estabilización de suelos. Se analizó en primer lugar la estabilización de un suelo arcilloso sin sulfatos del que derivó la publicación del artículo científico nº 3 de esta tesis; valorando la capacidad de activación del GGBS con MgO reciclado procedente de residuos de material refractario. Posteriormente se analizó la estabilización de un suelo con alto contenido en sulfatos mediante distintos cementantes, incluyendo varios basados en la activación del GGBS con MgO. El avance de esta parte de la investigación respecto a investigaciones previas reside en la realización y desarrollo de una zona de pruebas de campo, que consistió en el extendido, puesta en obra y estabilización de un suelo yesífero, delimitando

tramos de prueba donde se emplearon distintos cementantes basados en el uso de MgO, así como otros cementos comunes y cal. La zona de pruebas de campo fue ensayada y monitorizada durante varios meses, caracterizando la categoría de explanada alcanzada y su evolución en el tiempo. Esta fase de la investigación y pruebas de campo derivó en la publicación del artículo científico nº 4. Finalmente se analizó la estabilización en dos fases o procesos, de un suelo con alto contenido en sulfatos, realizando un pretratamiento para la formación controlada de etringita y una posterior estabilización mediante cementos basados en el uso de GGBS y MgO, publicando el artículo nº 5 de la presente tesis.

ABSTRACT

This thesis is a compendium of publications on the stabilisation of sulphate soils in the context of civil engineering using magnesium oxide (MgO)-based hydraulic cementitious agents. Previous research related to the use of a cement based on the activation of Ground Granulated Blast-furnace Slag (GGBS) through the addition of a low purity MgO has been developed and extended. The MgO used in this research comes from waste or co-products generated in the manufacturing processes and use of refractory material manufactured from the calcination of magnesite ore. The research carried out is based on previous research that led to the development of the aforementioned cementitious material patented jointly by the company Magnesitas Navarra S.A. (MAGNA) and the Public University of Navarra (joint UPNA/MAGNA patent "Hydraulic binder for construction materials"). This product has demonstrated a very high potential for its use in soil stabilisation, as well as a low reactivity with sulphates, being able to limit the adverse effects produced in the interaction between sulphates and stabilising additives based on calcium oxide (CaO) such as common cements and lime (the only stabilisers admitted in the national regulations for road construction), which results in the generation of hydrated sulphate-aluminates of the ettringite group, with a very high expansive capacity.

In this research, applications of hydraulic cements based on the use of different products and by-products rich in magnesium have been analysed, and the knowledge acquired has subsequently been transferred to their application as stabilisers for soils with high sulphate content. For this purpose, a field test area was developed. Thus, the research has been carried out in two blocks or global phases:

- A first one where cementitious agents based on the activation of GGBS with products, by-products and waste rich in MgO have been characterised; assessing the physical characteristics that these can develop in the production of mortars and artificial aggregates (granules), comparing these results with those obtained in other mortars and granules manufactured with a common cement. This phase of the research led to the publication of articles 1 and 2.
- The second phase of research was carried out on the application of magnesium-based cementitious agents for soil stabilisation. Firstly, the stabilisation of a clayey soil without sulphates was analysed, which led to the publication of scientific article no. 3 of this thesis, assessing the activation capacity of GGBS with recycled MgO from refractory material waste. Subsequently, the stabilisation of a soil with a high sulphate content was analysed using different cementitious agents, including several based on the activation of GGBS with MgO. The advance of this part of the research with respect to previous research lies in the performance of a field test, which consisted of the spreading, laying and stabilisation of a gypsiferous soil, delimiting test sections where different cementitious agents based on the use of MgO, as well as other common cements and lime, were used. The field test was tested and monitored for several months, characterising the category of levelling reached and its evolution over time. This phase

of the research and field test resulted in the publication of scientific article no. 4. Finally, the stabilisation of a soil with a high sulphate content was analysed in two phases or processes, carrying out a pre-treatment for the controlled formation of ettringite and a subsequent stabilisation by means of cements based on the use of GGBS and MgO, publishing article no. 5 of the present thesis.

BLOQUE A

1.- INTRODUCCIÓN

Esta sección introduce los aspectos generales, la contribución de la investigación a la Agenda 2030 y la relevancia de la investigación.

1.1.- ASPECTOS GENERALES

La estabilización de suelos en el ámbito de la ingeniería civil es una técnica constructiva de gran interés y mundialmente extendida debido a sus buenas propiedades técnicas, económicas y ambientales (Ceylan et al., 2015; Liu et al., 2019; Nagrale, Prashant P., & Patil, 2017). Esta técnica se emplea para mejorar la capacidad de los suelos utilizados en la formación de explanadas y terraplenes para la construcción de vías de comunicación. En muchos casos, la resistencia y otras características geotécnicas del terreno natural no cumplen con los requisitos de ingeniería necesarios para su empleo (derivando en problemas asociados a una alta plasticidad, elevada humedad, baja densidad, presencia de determinadas sales minerales...), lo que requiere la sustitución o estabilización del suelo. Sin embargo, reemplazar el terreno natural no apto puede resultar poco práctico debido a la disponibilidad de materiales, limitaciones de costos o regulaciones ambientales. La estabilización química del suelo surgió como una solución técnica y ambientalmente efectiva y rentable económicamente, para mejorar las propiedades geotécnicas de los suelos.

Si bien existen y se han estudiado técnicas de estabilización de suelos muy diversas (estabilización mecánica, estabilización con cementos, estabilización química, estabilización con material bituminoso, estabilización eléctrica...) (Afrin, 2017); la técnica más habitual es la adición de aditivos químicos. Actualmente es el Pliego de Prescripciones Técnicas Generales para obras de carreteras y puentes (PG-3), el documento técnico de referencia a nivel nacional. Este documento solo es de obligado cumplimiento para la realización de obras de carreteras dependientes del Ministerio de Transportes, Movilidad y Agenda Urbana (Ministerio de Fomento en el momento de su publicación). Sin embargo, la contrastada calidad técnica del mismo y ausencia de otra normativa ha llevado a que se tome como manual de referencia para todo tipo de estabilizaciones de suelos. El PG-3 en su capítulo 512 considera como aditivos estabilizantes las cales aéreas (definidas en la norma UNE-EN 459-1), los cementos comunes de clase resistente 32,5N (según UNE-EN 197-1), o los cementos especiales tipo ESP VI-1 de clase resistente 22,5N o 32,5 N. También indica que si el contenido ponderal de sulfatos solubles en el suelo a estabilizar (según norma UNE 103201), fuera superior al cinco por mil en masa, deberá emplearse un cemento resistente a los sulfatos, requiriendo de un estudio específico de aptitud de su uso.

El uso de los cementos comunes y la cal es particularmente adecuado en suelos arcillosos, que generalmente tienen propiedades inadecuadas como una alta plasticidad, mala capacidad de trabajo y baja capacidad de carga (Göktepe et al., 2008; Guney et al., 2007; Lin et al., 2007). Los suelos arcillosos consisten en minerales de aluminosilicatos con carga de superficie negativa que, por repulsión electrostática, mantienen una estructura abierta. Con la adición de cal o

cemento, se produce la fijación de iones de Ca^{2+} , se equilibran las cargas electrostáticas de las capas de arcilla y se reducen las fuerzas de repulsión electroquímica entre ellas. Esto provoca la adhesión de las partículas de arcilla mediante iones Ca^{2+} (floculación) en una estructura más granular (Kinuthia et al., 1999). Por otro lado, la adición de cal o cemento conlleva un aumento en la concentración de iones OH^- (e incremento de pH hasta valores en torno a 12), lo que resulta en la disolución de alúmina y sílice en la fracción de arcilla. La alúmina y sílice liberadas interactúan con iones de calcio para producir agentes cementantes (reacciones puzolánicas) (Yong & Ouhadi, 2007). Todos estos procesos dan como resultado un suelo con propiedades mejoradas: una estructura más granular, mayor permeabilidad y menor plasticidad (Lin et al., 2007; Wild et al., 1999). La mejora de las propiedades obtenidas dependerá de la cantidad y riqueza del aditivo, la mineralogía del suelo, el tamaño y la forma de sus partículas y las condiciones de curado (Göktepe et al., 2008; Misra et al., 2005; Yarbasi et al., 2007).

A pesar de las buenas características técnicas demostradas en el uso de aditivos a base de calcio como estabilizadores para suelos, la producción de cal y cemento han generado preocupaciones ambientales debido a su considerable consumo de energía y elevada huella de carbono, ya que estos productos proceden de la descarbonatación de rocas naturales que implica grandes emisiones de CO_2 a la atmósfera (Espuelas et al., 2018; Seco et al., 2012). Por otro lado, este tipo de tratamiento puede causar efectos adversos en algunos suelos e incluso llevar a la destrucción total de la estructura del material estabilizado. Una de las causas más comunes de este tipo de fallo es la presencia en el suelo a estabilizar del ion sulfato (SO_4^{2-}). El sulfato es un óxido muy común, tanto en suelos naturales alrededor de todo el mundo, como en los residuos industriales. Otras veces el sulfato puede proceder del agua utilizada para la compactación del suelo, o ser aportado por aguas de escorrentía o infiltradas en el entorno. Cualquiera que sea su origen, la reacción entre el calcio aportado por la cal o el cemento, el aluminio y el silicio aportados por los minerales arcillosos del suelo y el sulfato, todos juntos en presencia de agua, causa la formación de minerales expansivos, siendo el más común uno altamente hidratado y expansivo llamado etringita [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$] (Ciliberto et al., 2008; Crammond, 2002; Nobst & Stark, 2003; Norman et al., 2013). Si bien la mecánica de la formación de etringita no está bien establecida (Mohamed, 2000), sí se conocen las condiciones para su formación (Ouhadi & Yong, 2008), siendo estas: un pH alto, presencia de Al soluble, presencia de Ca soluble, presencia de sulfato soluble y disponibilidad de agua. También se sabe que la velocidad de formación de etringita se acelera debido a las altas temperaturas (Rajasekaran, 2005).

Por la conocida interacción entre el sulfato, la cal y el cemento que deriva en problemas de expansividad asociada a la formación de etringita, el PG-3 en su punto 512.3.3.3 hace referencia expresa a los suelos con sulfatos. En este punto se indica que cuando el suelo a estabilizar presente un contenido en sulfatos solubles superiores al 0,7%, se podrá hacer un estudio específico de aptitud de uso, limitando la expansión volumétrica del suelo estabilizado (según norma UNE-EN 13286-49). Aunque el PG-3 no prohíbe el uso de otros estabilizantes diferentes de la cal o el cemento, tampoco ofrece a los técnicos un soporte adecuado para la prescripción de otros tipos de estabilizantes, siendo el proyectista el responsable de la utilización de estos. Esto en la práctica supone una gran dificultad para el uso de cualquier estabilizante no

expresamente recogido en el PG-3 y por tanto el uso de manera casi exclusiva de la cal o el cemento. La ausencia de alternativas tecnológicas contrastadas para estabilizar los suelos con alto contenido en sulfatos provoca que en la práctica estos no puedan ser empleados en determinados tipos de usos en obra civil, recurriéndose en la mayoría de los casos a su sustitución por otros suelos aportados. Esto genera sobrecostes cuando no existe una fuente próxima de los suelos aportados necesarios, o la generación de impactos ambientales por la necesidad de explotación de nuevas graveras o canteras.

Una forma de reducir la formación de etringita en un suelo con sulfatos es mediante una sustitución parcial de cal o cemento por GGBS, un subproducto generado durante la producción de hierro en altos hornos, formado por la combinación de mineral de hierro con fundente calcáreo (C. Sekhar & Nayak, 2018; Wild et al., 1999). El GGBS contribuye con una gran cantidad de calcio, aluminio y silicio rápidamente disponibles en reacciones químicas, los cuales pueden ser activados con cal o cemento para formar geles cementantes, evitando o minimizando la formación de etringita. El estudio de este funcionamiento no está bien definido y sigue en estudio, pudiéndose producir un agotamiento del Ca disponible en el suelo, no quedando disponible para la formación de la etringita, desplazando a esta como principal mineral de la hidratación, algo que no consiguen por sí solos ni la cal ni el cemento. Este efecto protector contra el ataque de sulfatos se incrementa con la progresiva sustitución de cal con GGBS (Wild et al., 1999). Además, el GGBS también produce una matriz de cemento más densa, lo que reduce la permeabilidad y por lo tanto limita la disponibilidad de agua y la movilidad del sulfato en el suelo (Obuzor et al., 2011; Tasong et al., 1999; Wild et al., 1999).

Otra forma de estabilizar los suelos con sulfato puede ser el reemplazo de los aditivos a base de calcio por otros cationes metálicos, como el magnesio. Xeidakis (1996) demostró que la fijación de hidróxido de magnesio $[Mg(OH)_2]$ en las capas de arcilla expansivas es más rápida que la de hidróxido de calcio $[Ca(OH)_2]$, generando también su floculación. También demostró la capacidad de $Mg(OH)_2$ para aumentar el pH del suelo y la posibilidad teórica de generar geles cementantes a base de magnesio. Así, en los últimos años, ha habido un creciente interés en el potencial de los ligantes hidráulicos basados en MgO como una prometedora alternativa al cemento tradicional. Estos ligantes, que presentan MgO reactivo, tienen la capacidad de formar filosilicatos nanométricos poco ordenados conocidos como silicatos de magnesio hidratados (M-S-H), que poseen valiosas propiedades cementantes (Nied et al., 2016). Una fuente convencional de MgO es la roca de magnesita natural ($MgCO_3$), que se somete a una calcinación, un proceso en el que además de producir MgO, también libera cantidades significativas de CO_2 . La temperatura de calcinación desempeña un papel fundamental en la determinación de las propiedades del MgO resultante, influyendo en factores como el tamaño de cristal, la porosidad y el área superficial específica (Cao & Yan, 2019; Jin & Al-Tabbaa, 2013; Unluer, 2018). Durante este proceso de calcinación se produce un subproducto que consiste en polvo desprendido y recogido del interior del horno, rico en MgO potencialmente reactivo.

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con diferentes materiales basados en el MgO como estabilizantes de suelos, como respuesta a la necesidad del sector de la construcción por encontrar un ligante hidráulico para todo tipo de suelos. El fruto de este trabajo previo, realizado a escala de laboratorio, ha sido la patente conjunta UPNA/MAGNA "Ligante hidráulico para materiales de construcción" y diversos artículos científicos que se han publicado en revistas internacionales (Seco et al., 2012, 2017; Seco, Ramírez, Miqueleiz, García, et al., 2011).

Siendo la magnesita un recurso mineral limitado y costoso, consumido principalmente por la industria siderúrgica en forma de materiales refractarios, se siguen buscando aplicaciones innovadoras para los subproductos generados (como el polvo de horno de magnesia) así como para el MgO del material refractario agotado, que se integren en el modelo de producción y consumo de la economía circular. El uso de coproductos y residuos de MgO reduce considerablemente la carga medioambiental, ya que, aunque se generan importantes cantidades de CO₂ durante el proceso de fabricación de la magnesita calcinada, la huella de carbono corresponde al producto noble (refractario), siendo nula o muy reducida en los subproductos generados en el proceso o en los residuos que genera el material refractario agotado. Además, supondría la utilización de materiales que en la actualidad no tienen una valorización adecuada y acaban acopiados sin uso específico o en vertedero.

A pesar de todas las ventajas ya demostradas a nivel de laboratorio en el uso del MgO, su aceptación como parte de un aditivo estabilizante de suelos en el sector de la construcción está limitada por la falta de estudios técnicos concluyentes que permitan su inclusión en las diferentes normativas aplicables y la falta de productos comerciales disponibles en el mercado.

Uno de los problemas a los que se enfrenta el uso del MgO, es la reticencia que existe dentro del sector de la construcción debido a los inconvenientes derivados de la hidratación del MgO en los cementos. Pero hay que tener en cuenta que estos cementos presentan concentraciones de MgO hasta del 5% en masa admitido por la UNE EN 197-1, concentraciones muy superiores a las que se están experimentando para estabilizar los suelos, habiéndose utilizado en la presente investigación una concentración máxima del 2%. Investigaciones previas han valorado la capacidad de estabilización de suelos mediante adición de MgO reactivo y a través de procesos de carbonatación, pudiendo alcanzar un rango de resistencia similar al de los suelos estabilizados con cemento Portland (CP) (Yi et al., 2013).

La presente tesis da continuidad a estudios precedentes sobre la estabilización de suelos con sulfatos (Behnood, 2018; Celik & Nalbantoglu, 2013; McCarthy et al., 2012; Seco et al., 2017; Seco, Ramírez, Miqueleiz, & García, 2011), empleando cementantes basados en el magnesio, demostrando su eficacia en pruebas sobre diferentes materiales y entornos, incluyendo una prueba de campo estabilizando un suelo yesífero y obteniendo resultados concluyentes a una escala superior a la de laboratorio.

1.2.- CONTRIBUCIÓN DE LA INVESTIGACIÓN A LA AGENDA 2030 Y LA ECONOMÍA CIRCULAR

El empleo de subproductos y residuos de MgO, se alinea con el OBJETIVO 12 de los Objetivos de Desarrollo Sostenible (ODS) de la Agenda 2030 para el Desarrollo sostenible, adoptado en septiembre de 2015 por la Asamblea General de la ONU. La Agenda 2030 plantea 17 ODS con 169 metas de carácter integrado e indivisible que abarcan los ámbitos económico, social y ambiental. Las metas se dividen en dos tipos: las que marcan un hito a alcanzar, que se enuncian con números, y las enumeradas con letras, que son relativas a los medios de implementación. Los Estados miembros se comprometieron a movilizar los medios necesarios para su implementación mediante alianzas centradas fundamentalmente en la erradicación de la pobreza (Moran, 2020).



Figura 1. Objetivos de desarrollo sostenible de la Agenda 2030 (Gobierno de España, 2020).

El OBJETIVO 12 (PRODUCCIÓN Y CONSUMO RESPONSABLES) busca promover la gestión sostenible y el uso eficiente de los recursos naturales, reducir la generación de residuos y estimular la implementación de prácticas sostenibles en las empresas. Es uno de los ODS más transversales de la Agenda 2030, y trata de fomentar la transición de los modelos económicos, productivos y de consumo de los países más desarrollados hacia la sostenibilidad. Este ODS tiene varias metas, entre las que se encuentran las siguientes:

- Meta 12.5. Prevención, reducción, reciclado y reutilización de desechos. De aquí a 2030, reducir considerablemente la generación de desechos mediante actividades de prevención, reducción, reciclado y reutilización.
- Meta 12.C. Regulación de subsidios a combustibles fósiles. Racionalizar los subsidios ineficientes a los combustibles fósiles que fomentan el consumo antieconómico eliminando las distorsiones del mercado, de acuerdo con las circunstancias nacionales.

La investigación desarrollada en esta tesis también contribuye al cumplimiento de los requerimientos de la Ley 7/2022, de 8 de abril, de residuos y suelos contaminados para una economía circular. Esta Ley tiene por objeto sentar los principios de la economía circular a través de la legislación básica en materia de residuos, así como contribuir a la lucha contra el cambio

climático y proteger el medio marino. Dentro de estos objetivos el estudio de cementantes desarrollados a partir de subproductos y residuos de MgO se alinea con la operación de valorización R0505: Reciclado de residuos inorgánicos en sustitución de materias primas para la fabricación de cemento.

1.3.- RELAVANCIA DE LA INVESTIGACIÓN

En esta sección se expone la relevancia de la investigación fundamentada en dos aspectos: la presencia de suelos yesíferos y el uso de subproductos y residuos de óxido de magnesio.

La presencia de suelos yesíferos

La relevancia de la presente investigación incide directamente en el sector de la construcción y la ingeniería civil, quienes demandan la necesidad de encontrar un ligante hidráulico que posea unas prestaciones mecánicas similares, cuando no superiores a los cementantes normalizados, pero que sea medioambientalmente más sostenible.

También la aplicación directa de nuevos cementantes para la estabilización de suelos con sulfatos es a día de hoy un problema técnico sin resolver en la normativa española de obra civil. Lejos de lo que pueda parecer, los suelos con sulfatos son muy habituales en la superficie terrestre. El sulfato se presenta en el suelo formando mayoritariamente yeso como fase mineral más abundante. Los afloramientos de yeso son explotados en todo el mundo, siendo un mineral con múltiples usos y aplicaciones.

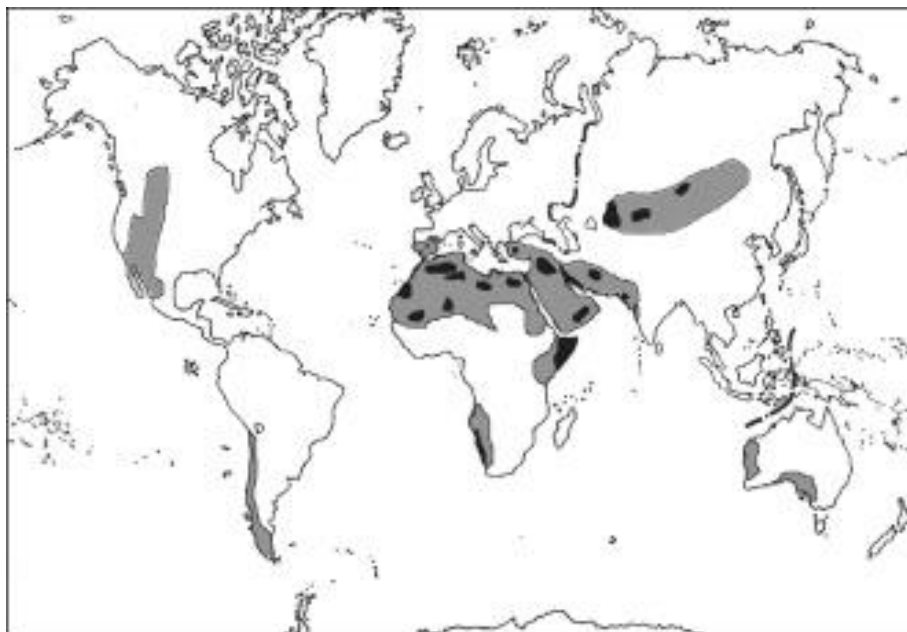


Figura 2. Mapa mundial de suelos yesíferos. En gris afloramientos de formaciones yesíferas (Escudero et al., 2015)

España se sitúa actualmente como el principal productor de yesos de Europa, siendo también uno de los principales del mundo, situándose en 2009 como el tercer productor mundial por detrás de China e Irán (Escavy et al., 2012). El yeso en España está principalmente formado parte de rocas sedimentarias evaporíticas aflorantes en diversas formaciones geológicas y extensas áreas, formando y generando suelos superficialmente (entendiendo como suelo un agregado de partículas sueltas, no cementadas).

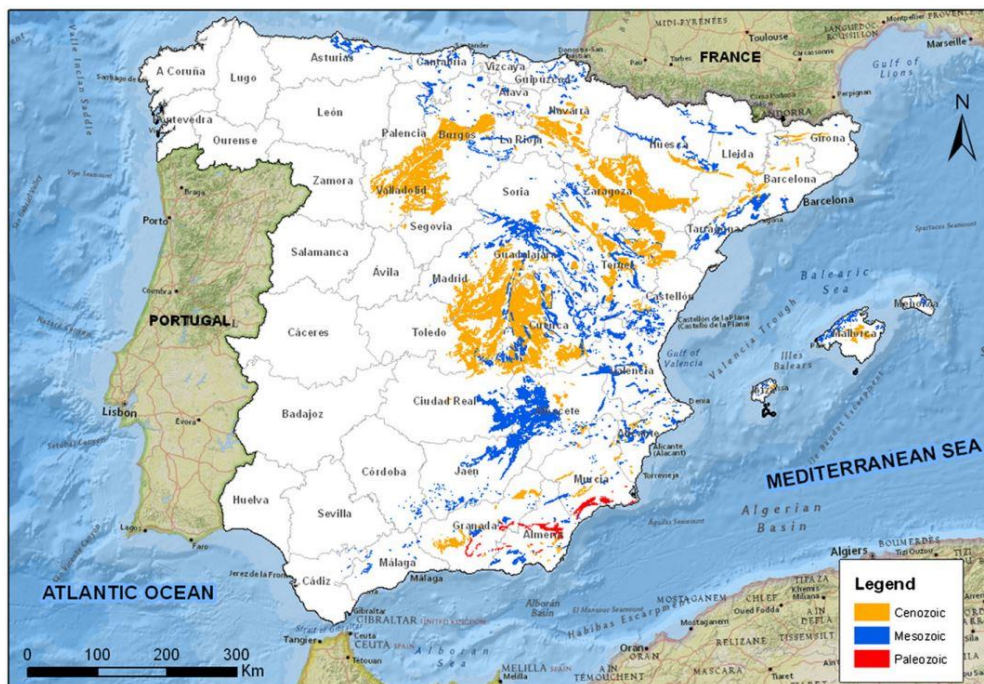


Figura 3. Afloramientos de unidades yesíferas en España (Escavy et al., 2012)

En total, son más de 21.000 km² la superficie de España donde afloran formaciones geológicas yesíferas (un 4,2% de su superficie), distribuidos fundamentalmente en la mitad oriental de la península (Escavy et al., 2012). A escala más local, en la Cuenca del Ebro los afloramientos de formaciones yesíferas alcanzan más de 4.600 km². Esta superficie se incrementa si se consideran suelos generados a partir de la denudación por meteorización de estos afloramientos, formando depósitos de suelos con alto contenidos de sulfatos en una extensión no definida a día de hoy.

El desarrollo y mantenimiento de caminos, vías, carreteras y obras de ingeniería en general a lo largo de esas áreas presenta actualmente la importante limitación del empleo de cementos u hormigones convencionales por la presencia de sulfatos. Los cementos sulforresistentes buscan mitigar el efecto adverso del sulfato sobre el hormigón modificando la composición química del cemento reduciendo el contenido en aluminato tricálcico (C₃A), incrementando la dosificación del cemento y reduciendo la permeabilidad de este (Prasad et al., 2006). Sin embargo, en la estabilización de suelos, la efectividad del empleo de cementos sulforresistentes ha resultado nula en la investigación realizada. En la fabricación de hormigones para ambientes agresivos por la presencia de sulfatos, se recurre a cementos sulforresistentes de elevadas resistencias y baja relación agua/cemento, pudiendo deducirse que la resistencia del hormigón al ataque por sulfatos puede

depender en gran medida de una elevada densidad y baja permeabilidad, y no tanto de la ausencia de reacciones químicas para formar etringita. En los suelos estabilizados no es posible llegar a los altos valores de densidad y baja permeabilidad de los hormigones, donde la formación o no de etringita quedará condicionada fundamentalmente por las reacciones químicas que en ellos se produzcan. Estas limitaciones podrían ser solventadas con el empleo de cementantes alternativos como los analizados en la presente tesis.

Valorización de subproductos y residuos de MgO

Otro aspecto en el que incide directamente la presente tesis es en la búsqueda de usos y aplicaciones de subproductos y residuos generados en la producción de material refractario de MgO.

La empresa MAGNA, manufactura en su planta situada en la localidad de Zubiri (Navarra), refractario de MgO a partir de la calcinación de magnesita y de dolomita en menor medida. Utiliza para ello hornos rotatorios de gran capacidad, alcanzando en función del productor final requerido, temperaturas de 1300° o 1800° C.

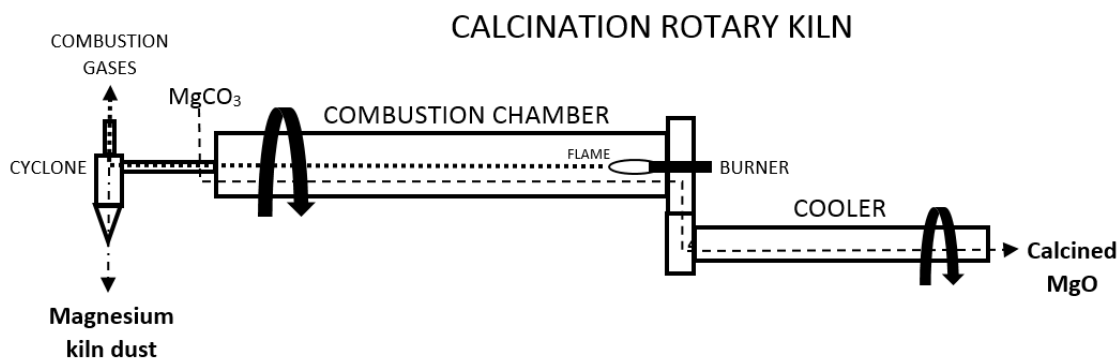


Figura 4. Esquema simplificado del proceso de obtención del MgO a partir de magnesita

En este proceso de calcinación, los gases de combustión arrastran el polvo generado en el horno, recogiénolo en un separador ciclónico. Este material es considerado un subproducto de baja comercialización hoy en día, denominado PC-8. El PC-8 es la fuente de MgO utilizada en la patente conjunta UPNA/MAGNA "Ligante hidráulico para materiales de construcción". Este material también ha sido utilizado en la presente investigación. El PC-8 tiene un contenido variable de MgO (en torno al 60%) pero no todo está en forma de óxido, parte se encuentra sin descarboxar, considerándose un material moderadamente reactivo. En la planta de Zubiri, La producción media de los últimos años de este subproducto es de 20.000 T/año. También se ha utilizado en la presente investigación el polvo recogido en el separador ciclónico de una planta que MAGNA posee en la localidad de Calanda (Teruel), donde es denominado PC-Calanda, produciéndose unas 25.000 T/año. La investigación desarrollada también ha empleado un polvo obtenido como subproducto tras la desulfuración con hidróxido cálcico de los gases de combustión de los hornos rotativos, denominado

Sulfamag. Este material tiene un porcentaje de MgO alrededor de 33% y un contenido en sulfato de calcio del orden del 28% generado en la desulfuración por vía seca.

Para el desarrollo de la presente tesis también se han empleado residuos refractarios de MgO. En la Unión Europea (UE), se estima que la producción de materiales refractarios gastados o agotados está entre 1,42 y 2,66 millones de toneladas al año. Estos residuos carecen de métodos efectivos de valorización (Arianpour et al., 2010; Conejo et al., 2006; Silva et al., 2017). De estos residuos, el 26% corresponde a materiales refractarios reciclados de dolomita y magnesita (DMRR) de la industria del acero (Horckmans et al., 2019). Esto representa una disponibilidad potencial de 0,43 a 0,80 millones de toneladas por año solo en la UE. Los DMRR podrían convertirse en componentes para la producción de aglomerantes de MgO debido a su alto pH y su contenido reactivo de MgO, cal libre (CaO) y silicato dicálcico (C₂S) (Fang et al., 1999; Horckmans et al., 2019).

2.- CONTEXTO DE LA INVESTIGACIÓN

Como se ha citado anteriormente, la presente tesis doctoral se ha desarrollado dentro del grupo de investigación "Proyectos, Ingeniería Rural y Energías Renovables" de la Universidad Pública de Navarra (UPNA). Desde el inicio de la actividad de este equipo, la principal línea de investigación ha sido la reutilización de residuos y subproductos industriales de naturaleza inerte, para su empleo en el sector de construcción, como componentes parciales o totales de diferentes materiales y en distintas aplicaciones tales como la estabilización de suelos, la fabricación de materiales de cerramiento de edificaciones, la producción de materiales de construcción prefabricados no estructurales o la fabricación de ligantes hidráulicos.

Dentro de este contexto y durante la realización de la presente tesis doctoral se han desarrollado los siguientes proyectos de investigación:

Año	Título del proyecto/contrato de investigación	Organismo financiador
2022	Cemento supersulfatado: un nuevo cemento sostenible para el sector de la Construcción en la Europa del S XXI (CEMEGREEN)	Plan Estatal de Investigación Científica y Técnica y de Innovación
2022	Análisis de la aptitud de los residuos relaves y botaderos de las Explotaciones Mineras La Poderosa / Condestable / San Vicente / SIMSA para la fabricación de materiales de construcción sostenible en Perú.	Xenera S.A.C
2022	Propuesta de campaña experimental para el estudio del potencial de lixiviación de residuos en aplicaciones ambientales.	Gestión Ambiental de Navarra, S.A.
2021	Desarrollo de un método acelerado para el estudio del potencial de lixiviación de metales pesados de residuos en construcción y actuaciones medioambientales en Navarra (LIXINAV).	Departamento de Desarrollo Rural y Medio Ambiente. Gobierno de Navarra
2021	Realización de campaña para la obtención de formulaciones de hormigones de material reciclado y de densidad superior a 2.500 kg/m ³ .	Escaleras Aguerri S.L.
2021	Investigación avanzada en el ámbito de los residuos industriales de base mineral como materias primas secundarias para la formulación de nuevos productos ecológicos y la creación de bucles de economía circular (CERES)	Magnesitas Navarras S.A.
2019	Estudio básico para la estabilización de suelos con alto contenido en sulfatos acopiados en el Pol. Industrial	NASUVINSA Navarra de Suelo y Vivienda, S.A.

de Lekunberri (Navarra), y su empleo en obras de movimiento de tierras.

2019 Fomento de la economía circular en la valorización de materiales refractarios. Magnesitas Navarras, S.A.

2018 Estudio y aplicación de coproductos basados en el óxido de magnesio como estabilizadores de suelos con contenido en sulfatos. Magnesitas Navarras, S.A.

3.- OBJETIVOS DE LA INVESTIGACIÓN

El **objetivo general** de la presente tesis es ampliar la investigación y validar la capacidad estabilizante de suelos con alto contenido en sulfatos mediante el empleo de cementantes hidráulicos basados en el uso de productos con alto contenido en óxido de magnesio. La fuente de este MgO son residuos o subproductos del procesamiento de mineral de magnesita para la fabricación de productos refractarios.

Este objetivo general pretende cubrir dos aspectos: por un lado, se plantea como una aportación a la búsqueda de solución a un antiguo problema de la ingeniería civil desarrollado en terrenos donde existen suelos con sulfatos y en segundo lugar como una aportación a la búsqueda de cementantes alternativos basados en el MgO que pueden incorporarse a las diferentes legislaciones en el ámbito de la construcción y la ingeniería civil, posibilitando además la valorización de grandes cantidades de MgO procedentes de subproductos y residuos de la industria refractaria.

Este objetivo general se ha dividido en dos **objetivos específicos**:

- 1) **OBJETIVO ESPECÍFICO 1.** Comprobar y verificar la capacidad cementante y el comportamiento mecánico de cementos basados en el empleo de GGBS y óxidos de magnesio (aportados por subproductos generados en la calcinación de magnesita o por residuos refractarios con base magnesio), en comparación con un cemento común (según UNE-EN 197-1). Para ello se ha seguido una metodología basada en ensayos físicos y químicos de laboratorio sobre morteros y gránulos reciclados, centrados fundamentalmente en la caracterización y análisis de parámetros resistentes.
- 2) **OBJETIVO ESPECÍFICO 2.** Comprobar, analizar y parametrizar el efecto de cementantes hidráulicos basados en magnesio, aplicados en la estabilización de suelos con alto contenido en sulfatos. Para ello se ha seguido una metodología basada en ensayos de laboratorio sobre un suelo arcilloso sin sulfatos estabilizado, en ensayos de laboratorio y de campo ejecutados en una zona de pruebas desarrollada para ello, estabilizando un suelo con alto contenido en sulfatos; y en la estabilización de un suelo con sulfatos pretratado y estabilizado.

4.- METODOLOGÍA DE LA INVESTIGACIÓN

El presente punto recoge la metodología de la investigación realizada.

4.1.- ESTUDIO BIBLIOGRÁFICO

El inicio fundamental del proceso de desarrollo de la presente tesis doctoral implicó la recopilación y estudio de la bibliografía existente relacionada con el tema central de la investigación. Este paso requirió de un examen y análisis de las diversas metodologías empleadas, así como de los resultados obtenidos en investigaciones previas y estudios relacionados. A través de la exploración de la literatura científica existente, se buscó identificar las lagunas de conocimiento, las tendencias previas de investigación y perspectivas actuales del campo de estudio.

Parte de esta labor de revisión y análisis se refleja en la primera parte de esta tesis, donde se establecen los fundamentos teóricos y se contextualiza la importancia del tema de investigación. Además, esta revisión bibliográfica se extendió a lo largo de los diferentes artículos científicos que conforman la presente tesis doctoral.

El proceso inicial de recopilación y análisis de la bibliografía existente sentó las bases y aportó la perspectiva que dio enfoque y desarrolló la tesis doctoral.

4.1.- CAMPAÑA EXPERIMENTAL

Según los objetivos definidos de la investigación y a partir de la bibliografía analizada y experiencias previas del grupo de investigación en que se ha desarrollado esta tesis, se ha seguido una campaña experimental fundamentada en el estudio mediante ensayos físicos de las características resistentes de distintos cementantes hidráulicos basados en el empleo de MgO, en situaciones o aplicaciones diversas. Esta campaña experimental ha seguido las siguientes fases:

- **FASE 1.** En esta fase se ha estudiado y analizado la capacidad cementante y el comportamiento de cementos hidráulicos basados en el empleo de GGBS y óxidos de magnesio procedentes de subproductos de la calcinación de la magnesita y de residuos de material refractario agotado, mediante su uso en la fabricación de morteros y de gránulos reciclados para su empleo como áridos ligeros. Esta 1^a fase de investigación ha derivado en la publicación de los artículos 1 y 2 que conforman parte de esta tesis, titulados:
 - *"Assessment of the ability of MgO based binary binders for the substitution of Portland cement for mortars manufacturing".*
 - *"Recycled granulates manufacturing from spent refractory wastes and magnesium based binder".*
- **FASE 2.** En esta fase se ha estudiado el comportamiento de un suelo arcilloso (sin sulfatos), estabilizado mediante el empleo de GGBS aditivado con residuos de material refractario con alto contenido en magnesio; cuantificando parámetros resistentes y capacidad expansiva. Esta 2^a fase de investigación ha derivado en la publicación del artículo nº 3 que forma parte de la presente tesis, titulado:

- *"Stabilization of a Clay Soil Using Cementing Material from Spent Refractories and Ground-Granulated Blast Furnace Slag"*.
- **FASE 3:** En esta fase se ha estudiado y analizado la estabilización de dos suelos arcillosos con alto contenido en sulfatos, mediante el empleo de cementantes hidráulicos basados en el empleo de GGBS y óxidos de magnesio procedentes de subproductos de la calcinación de la magnesita. Estos resultados se han comparado realizando la estabilización con un aditivo rico en sílice y aluminio (filler de aluminio), y con cementantes habituales en la estabilización de suelos: cal y cemento común. Esta fase de investigación se llevó a cabo sobre muestras de laboratorio y mediante ensayos en una zona de pruebas de campo preparada a tal efecto. Esta 3^a fase de investigación ha derivado en la publicación de los artículos nº 4 y 5 que conforman parte de esta tesis, titulados:
 - *"Sulphate soil stabilisation with magnesium binders for road subgrade construction"*.
 - *"Experimental Study of the Valorization of Sulfate Soils for Use as Construction Material"*.

4.3.- ANÁLISIS DE RESULTADOS

En cada uno de los artículos científicos contenidos en la presente tesis, producto de la campaña experimental planteada, se realiza un análisis de los resultados obtenidos en comparación con resultados bibliográficos y experiencias previas, resumiéndose los aspectos más relevantes de estos en el siguiente punto.

5.- RESUMEN DE RESULTADOS

En este punto de la tesis se exponen de forma sintética, los materiales, la metodología, los resultados y conclusiones obtenidos en cada uno de los artículos científicos publicados. Los artículos se incluyen íntegramente en el punto 8 del BLOQUE B de la presente tesis.

5.1.- CAMPAÑA EXPERIMENTAL FASE 1: ARTÍCULOS 1 Y 2

5.1.1.- ARTÍCULO 1: *Análisis de la capacidad de ligantes binarios a base de MgO para sustituir al cemento Portland en la fabricación de morteros*

Introducción

En este artículo se ha evaluado la capacidad cementante de un polvo de horno de magnesia (PC-8) y un MgO calcinado comercial (MCB100), combinados con GGBS, como constituyentes de ligantes hidráulicos binarios M-S-H (silicatos de magnesio hidratados). La investigación se llevó a cabo en laboratorio mediante la fabricación de pastas de cemento y morteros.

Materiales empleados

Para la fabricación de los morteros se utilizó como árido una arena calcárea comercial de 0-4 mm procedente de roca caliza triturada. Para la formulación de los cementantes se utilizaron dos fuentes de MgO. Por un lado, un MgO comercial de alta reactividad obtenido de rocas de magnesita calcinadas a 1.100 °C, comercializado con el nombre de MCB100 por la empresa Magnesitas Navarras S.A. (MAGNA) situada en Zubiri (Navarra). El segundo material fue el PC-8 (ver punto 1.3.)

El GGBS es un subproducto obtenido durante la fabricación del arrabio. Se forma por enfriamiento rápido de la escoria de hierro fundido para mantener una estructura amorfa, triturándose posteriormente para aumentar su reactividad. El GGBS empleado para esta investigación fue suministrado por Heidelberg Cement Group (Reino Unido).

El cemento Portland (PC) utilizado en esta investigación es un cemento comercial fabricado de acuerdo con norma europea EN 197-1, identificado como CEM II/B-L 32.5 N.

En la Tabla 1 se muestra la composición química y los parámetros representativos de la reactividad de los cementantes empleados.

ÓXIDOS (%)	PC-8	MCB100	GGBS	PC
MgO	59,67	82,26	9,05	1,21
CaO	9,1	3,79	43,94	70,82
SO ₃	6,27	0,21	2	4,15
SiO ₂	2,8	3,41	32,18	14,12
Fe ₂ O ₃	2,34	2,9	0,33	4,1
Al ₂ O ₃	0,57	0,82	10,4	3,36
Pérdida al fuego a 1,050 °C	19,25	6,61	0,46	4,97
Reactividad en ácido cítrico (min)	29	2	>600	>600
pH en agua	10,66	10,88	9,82	11,88
Cal libre (%)	0,81	1,04	0,28	3,67

Tabla 1. Composición química, finura y reactividad de los cementantes

En la Figura 5 se muestra la granulometría de los componentes de los ligantes considerados para la investigación de laboratorio.

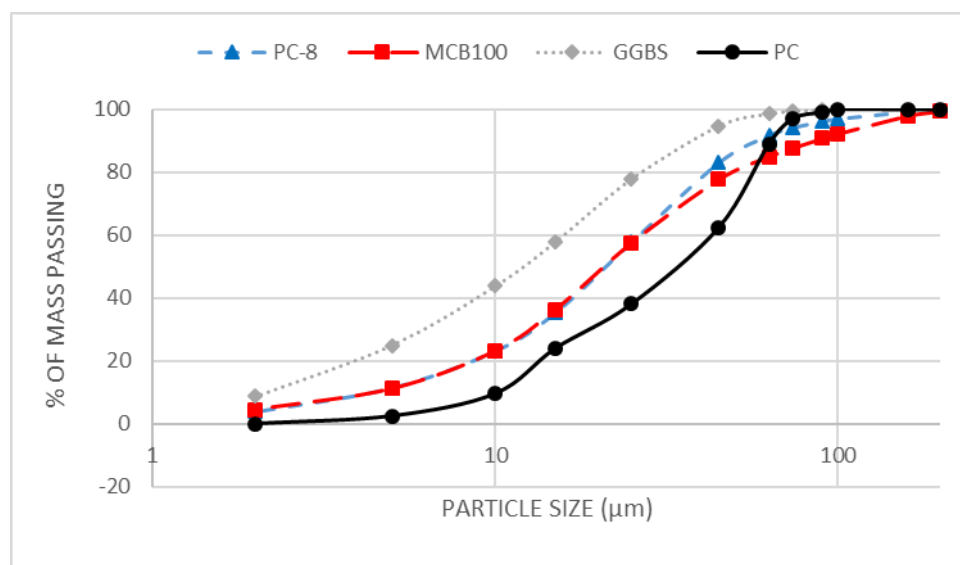


Figura 5. Curvas granulométricas de los cementantes

Tipos de muestras analizadas y métodos

Para la investigación de laboratorio se fabricaron pastas de cemento (cementante + agua) y morteros (cementante, agua y árido).

Sobre las pastas se realizaron ensayos de difracción de rayos X (DRX), termogravimetría y pH a las edades de 28 y 90 días, tras curado en inmersión de agua.

Los morteros se caracterizaron mediante ensayos de consistencia en fresco, tiempos de fraguado (inicio y fin de fraguado) y resistencia a flexión y compresión sobre probetas prismáticas de 4x4x16 cm, tras 7, 14, 21, 28 y 90 días de curado en inmersión en agua.

Para la fabricación de los cementantes alternativos al cemento Portland se eligió una relación en peso MgO / GGBS = 20/80.

En las pastas y las muestras de mortero fabricadas con cemento Portland, la proporción de agua respecto a cemento se fijó en 1/2,5 (w/c = 0,4). Para las muestras de morteros con cementantes de MgO la relación agua/aglomerante se fijó en 1/1,5 (w/b = 0,6) debido a las necesidades de trabajabilidad de estos morteros de productos de MgO.

Análisis de resultados y conclusiones

De la investigación realizada se desprenden como más relevantes las siguientes consideraciones:

- Los morteros empleados presentaron variaciones de consistencia y tiempos de curado, acordes a diferencias granulométricas de los cementantes, a pequeñas variaciones de su pH y a las variaciones de reactividad y velocidad de hidratación. Los morteros de MgO mostraron una reactividad más lenta y progresiva que el PC, con mayores tiempos de fraguado y mayor consistencia.

Ensayo	Cementante		
	PC-8 + GGBS	MCB100 + GGBS	CEM II 32.5
Consistencia en mesa de sacudidas (mm)	160	144	177
Tiempos de fraguado (min)			
Inicial	458	478	200
Final	1261	1450	317
Densidad seca (g/cm ³)	1,88	1,88	1,96
pH en agua			
28 días	11,43	11,47	12
90 días	11,49	11,7	12,09

Tabla 2. Resumen de valores de consistencia, tiempos de fraguado, densidad seca y pH

- Del estudio de los resultados obtenidos en los ensayos DRX y termogravimetrías, pudo determinarse la presencia de geles derivados de las reacciones puzolánicas del Mg (MgO, Mg(OH)₂, MgCO₃ y CaCO₃), y la presencia de M-S-H en las pastas de cemento, manteniendo de nuevo una coherencia con las diferencias de reactividad de los cementantes empleados. Las pruebas XRD demostraron la capacidad de los productos de MgO para hidratar y formar geles M-S-H. La prueba TG/DTG mostró diferencias en los procesos de deshidratación, deshidroxilación y descarbonatación entre los sistemas M-S-H y C-S-H de los conglomerantes.

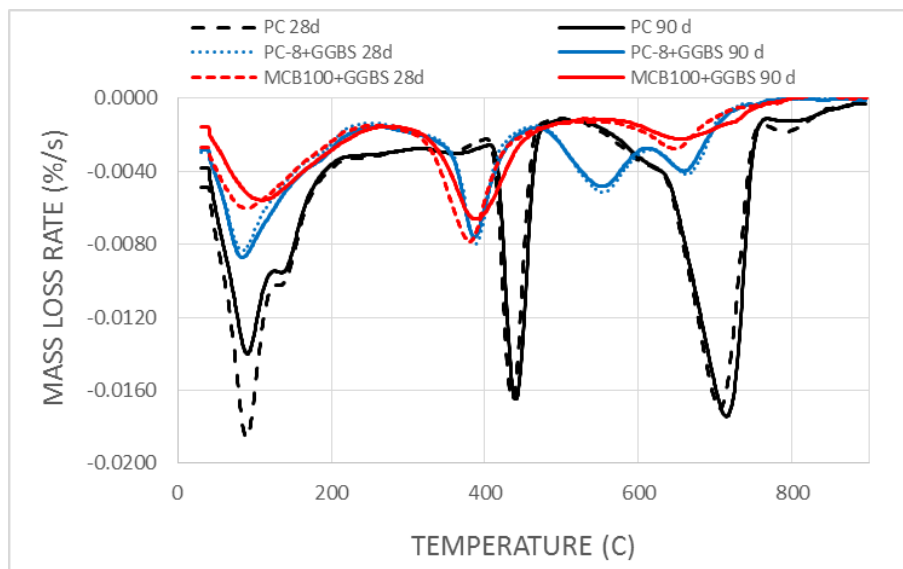


Figura 6. Curvas termogravimétricas DTG sobre muestras de pastas de cemento

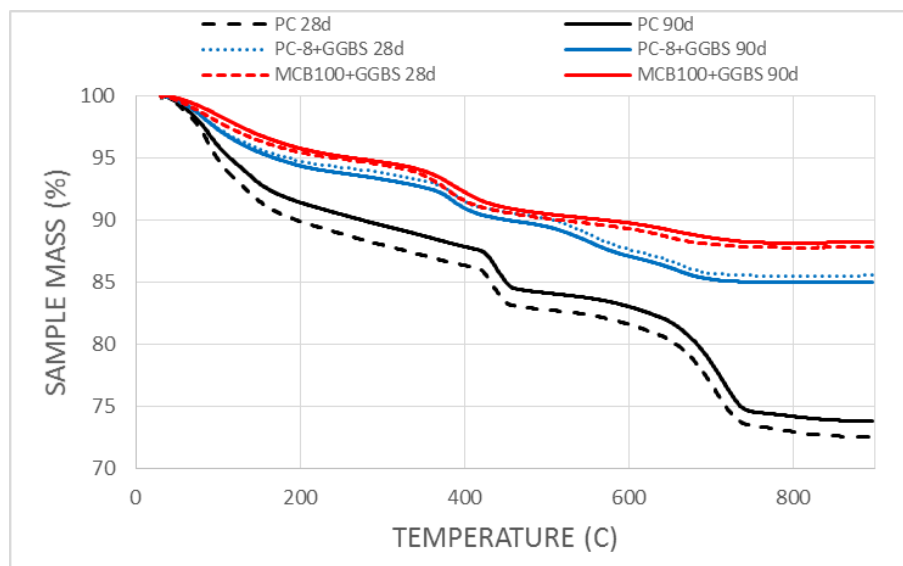


Figura 7. Curvas termogravimétricas TG sobre muestras de pastas de cemento

- El aspecto más reseñable y evidente de los ensayos realizados, son los resultados de resistencia obtenidos a flexión y compresión de los morteros fabricados (ver figuras 8 y 9). Respecto a los ensayos de resistencia a flexión, el mortero de PC mostró un rápido desarrollo de la resistencia debido a su rápida hidratación y alta reactividad. A los 7 días alcanzó una resistencia de 4,51 MPa a flexión que aumentó lentamente hasta 5,25 MPa a los 90 días. Los morteros de MCB100 + GGBS y PC-8 + GGBS mostraron un aumento directo de la resistencia a la flexión y compresión a lo largo del tiempo de curado. Así, mientras que a la edad de 7 días, los morteros MCB100 + GGBS y PC-8 + GGBS alcanzaron valores de resistencia a flexión entre un 25% y un 50% de la obtenida por PC, a la edad de 90 días estos valores superaron al obtenido por el PC, alcanzando el mortero MCB100 + GGBS los 6,49 MPa y el mortero PC-8 + GGBS los 7,14 MPa, frente a los 5,25 MPa del PC. La menor resistencia a la flexión de los morteros a base de MgO a las primeras

edades de curado se debe probablemente a la capacidad de hidratación más lenta y a la reactividad de estos ligantes, tal y como se desprende del ensayo de tiempos de fraguado y de acuerdo con los resultados obtenidos por Jin y Altabaa (2014) y Bernard et al. (2017). Considerando las temperaturas de calcinación, los parámetros de reactividad y finura de PC-8 y MCB100, la mayor resistencia a la flexión alcanzada por las muestras de PC-8 + GGBS en comparación con las de MCB100 + GGBS es un resultado inesperado, ya que el MCB100 presenta MgO más reactivo. Esta mayor resistencia podría estar relacionado con el contenido de CaO del PC-8 que se hidrataría para formar geles C-S-H contribuyendo a aumentar la resistencia a la flexión de las muestras de PC-8 + GGBS (Bernard et al., 2017).

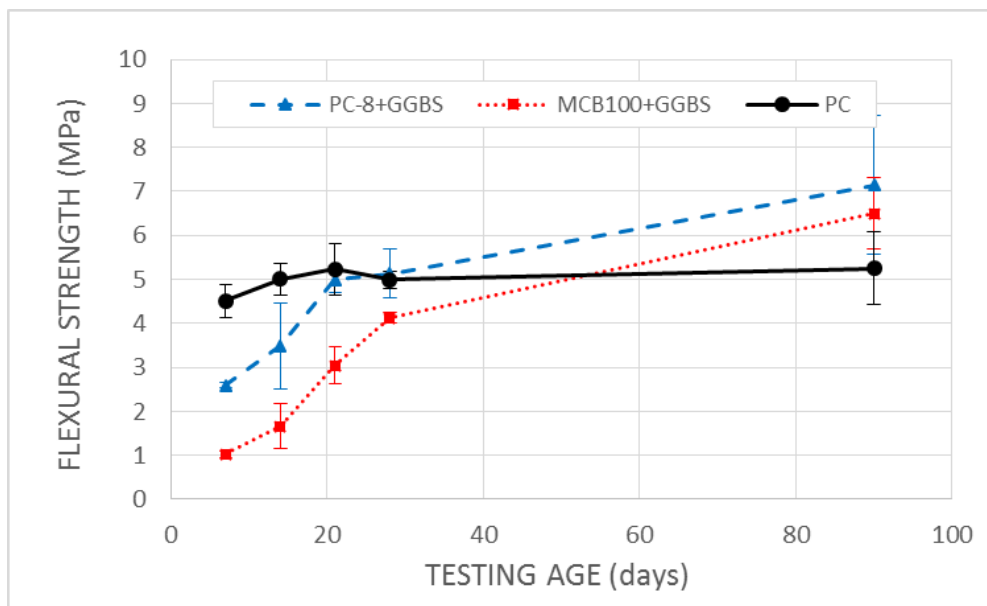


Figura 8. Resistencia a flexión de morteros

- En cuanto a la resistencia a compresión simple, el mortero de PC alcanzó una resistencia a la compresión de 23,11 MPa a la edad de 7 días que aumentó hasta 27,90 MPa a los 90 días. Este escaso incremento de la resistencia a la compresión concuerda con lo observado en el ensayo de flexión, poniendo de nuevo en relieve la rápida hidratación del PC en comparación con los ligantes binarios MgO-GGBS. Los morteros de MCB100 + GGBS y PC-8 + GGBS mostraron un desarrollo de la resistencia a la compresión cercano al observado en la resistencia a la flexión debido a la formación de geles puzolánicos (Dave et al., 2016; Huynh et al., 2018; Namarak et al., 2017). Al igual que en el ensayo de resistencia a flexión, el mortero de PC-8 + GGBS mostró una mayor resistencia a la compresión que MCB100 + GGBS en todas las edades de curado. Estos valores aumentaron a lo largo del tiempo de curado hasta alcanzar 19,36 MPa para el MCB100 y 31,68 MPa para el PC-8 a los 90 días. El mortero de GGBS + PC-8 superó la resistencia a la compresión del PC a la edad de 90.

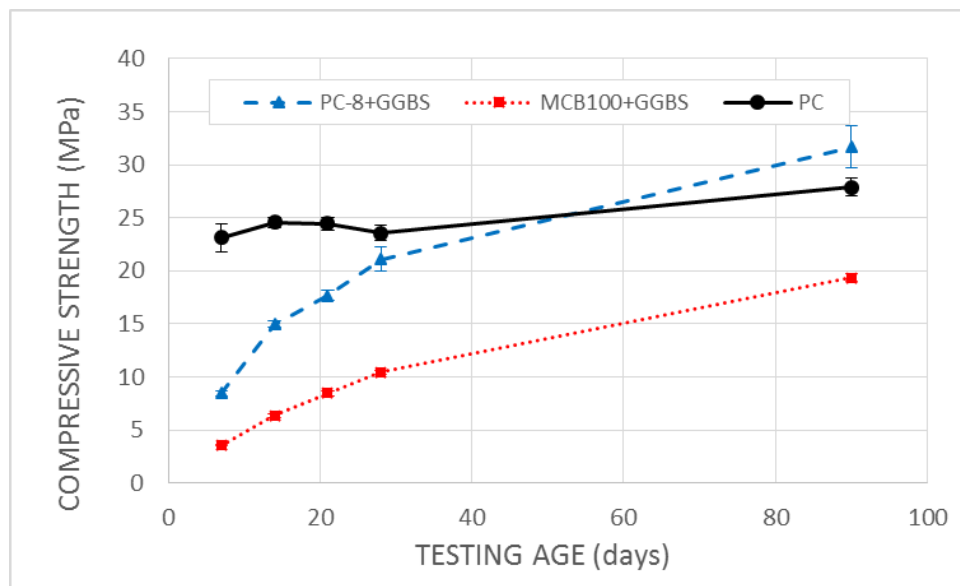


Figura 9. Resistencia a compresión de morteros

- Los resultados de las pruebas de resistencia a flexión y compresión demostraron la capacidad de los ligantes binarios MgO + GGBS para la fabricación de morteros ordinarios de albañilería con las propiedades mecánicas requeridas. También se demostró en esta investigación la mayor capacidad del PC-8, un coproducto, en comparación con MCB100, un producto comercial de MgO reactivo, para formar geles hidráulicos cementantes, alcanzando mayor resistencia mecánica que el PC. También se ha demostrado las buenas propiedades mecánicas de los sistemas M-S-H en comparación con los C-S-H a edades de curado largas, y la conveniencia de PC-8 en comparación con MCB100 para generar cementantes con GGBS.

5.1.2.- ARTÍCULO 2. Fabricación de gránulos reciclados a partir de residuos refractarios y cementantes basados en magnesio

Introducción

En este artículo se ha evaluado la capacidad cementante de GGBS + PC8, para la formación de gránulos reciclados para su empleo en construcción según EN 13055, a partir de dos residuos secundarios refractarios de magnesio (SRW). Se valoró también la influencia de la atmósfera de curado de los gránulos producidos, empleando tres tipos de ambientes: aire, una atmósfera con 20% CO₂ - 80% N₂ y en una atmósfera de 100% de CO₂. Para caracterizar los gránulos se realizaron ensayos de granulometría, análisis térmico, densidad de partículas, densidad aparente, absorción de agua y resistencia mecánica.

Materiales empleados

Los residuos refractarios de magnesio empleados en la presente investigación, proceden de altos hornos para la producción de acero. En este trabajo se emplearon dos tipos de SRW, denominados respectivamente P1 y P2. El P1 se genera durante el proceso de recuperación del refractario que protege un horno de cuchara (donde se obtienen acero fundido). El P2 proviene de la demolición del refractario de un recipiente de distribución de acero fundido denominado artesa o "tundish".

Como conglomerante hidráulico se empleó de nuevo la combinación GGBS + PC8 también en una proporción de 80 a 20, en base a experiencias previas.

Composición química (Fluorescencia RX)				
%	P1	P2	PC-8	GGBS
SiO ₂	2,07	16,53	2,8	32,18
CaO	3,49	12,51	9,1	43,94
Fe ₂ O ₃	1,16	10,99	2,34	0,33
Al ₂ O ₃	2,81	13,69	0,57	10,4
SO ₃	0,16	0,31	6,27	2
Cr ₂ O ₃	0,04	0,43	-	-
P ₂ O ₅	0,14	0,09	-	-
MnO	0	1,95	-	-
MgO	76,13	41,11	59,67	0,25
Reactividad				
Pérdida al fuego 1050°C (%)	14	1,86	19,25	0,46
Cal libre (%)	0,84	-	1,32	0,28
Reactividad (min)	>1200	>1200	>1416	>480
pH	11,37	11,69	10,66	9,82

Tabla 3. Composición química, reactividad y mineralogía de los residuos refractarios y cementante

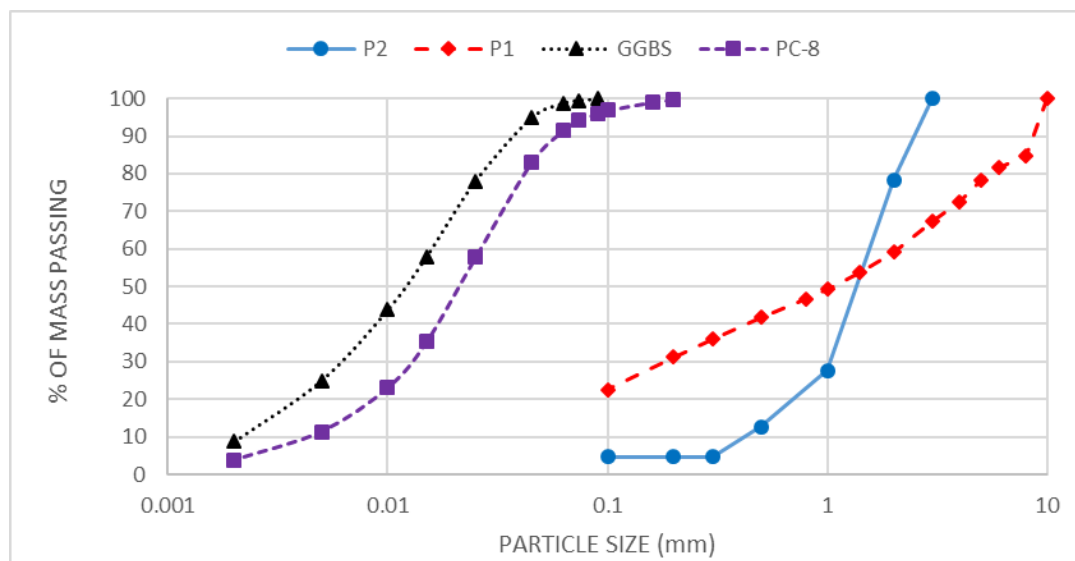


Figura 10. Curvas granulométricas de los residuos refractarios y constituyentes del cementante hidráulico

Tipos de muestras analizadas y métodos

Para la fabricación de los gránulos se empleó una granuladora, de 600 mm de diámetro equipada en su interior con una pala. Los residuos refractarios y el cementante, se premezclaron en seco previamente, antes de su introducción en la granuladora. Las proporciones de residuos frente aglutinantes consideradas fueron 90 a 10, 80 a 20 y 70 a 30. Una vez puesto en marcha la granuladora, se roció agua desionizada a lo largo de un minuto, manteniendo el proceso de granulación durante 10 minutos. Este procedimiento se repitió varias veces para cada combinación, para obtener la cantidad necesaria de gránulos para su ensayo. Posteriormente, los gránulos fueron recogidos y curados en atmósfera compuestas por aire, por 20 % CO₂ - 80 % N₂, y por 100 % CO₂, hasta las edades de ensayo de 7 y 28 días.

Se fabricaron un total de 36 combinaciones, según la tabla 4. Cada combinación fue designada por el código SRW/BP/CT/CA siendo:

- ✓ Tipo de residuo SRW (P1, P2).
- ✓ Porcentaje de aglutinante BP (10 %, 20 %, 30 %).
- ✓ Tiempo de curado TC (7 días, 28 días).
- ✓ Atmósfera de curado CA (aire, CO₂ 20 %-N₂ 80%, CO₂ 100 %).



Fotografía 1. Aspectos de los gránulos, sobre bandejas de 30x50 cm

Combinación	Tipo de SRW	SRW (g)	Cementante (g)	Agua (g)	Tiempo de curado (días)	Atmósfera de curado
P1/10/7/A	P1	900	100	200	7	Aire
P1/20/7/A	P1	800	200	200	7	
P1/30/7/A	P1	700	300	200	7	
P1/10/28/A	P1	900	100	200	28	
P1/20/28/A	P1	800	200	200	28	
P1/30/28/A	P1	700	300	200	28	
P1/10/7/C20	P1	900	100	200	7	CO ₂ 20% N ₂ 80%
P1/20/7/ C20	P1	800	200	200	7	
P1/30/7/ C20	P1	700	300	200	7	
P1/10/28/ C20	P1	900	100	200	28	
P1/20/28/ C20	P1	800	200	200	28	
P1/30/28/ C20	P1	700	300	200	28	
P1/10/7/C100	P1	900	100	200	7	CO ₂ 100%
P1/20/7/ C100	P1	800	200	200	7	
P1/30/7/ C100	P1	700	300	200	7	
P1/10/28/ C100	P1	900	100	200	28	
P1/20/28/ C100	P1	800	200	200	28	
P1/30/28/ C100	P1	700	300	200	28	
P2/10/7/A	P2	900	100	200	7	Aire
P2/20/7/A	P2	800	200	200	7	
P2/30/7/A	P2	700	300	200	7	
P2/10/28/A	P2	900	100	200	28	
P2/20/28/A	P2	800	200	200	28	
P2/30/28/A	P2	700	300	200	28	
P2/10/7/C20	P2	900	100	200	7	CO ₂ 20% N ₂ 80%
P2/20/7/ C20	P2	800	200	200	7	
P2/30/7/ C20	P2	700	300	200	7	
P2/10/28/ C20	P2	900	100	200	28	
P2/20/28/ C20	P2	800	200	200	28	
P2/30/28/ C20	P2	700	300	200	28	
P2/10/7/C100	P2	900	100	200	7	CO ₂ 100%
P2/20/7/ C100	P2	800	200	200	7	
P2/30/7/ C100	P2	700	300	200	7	
P2/10/28/ C100	P2	900	100	200	28	
P2/20/28/ C100	P2	800	200	200	28	
P2/30/28/ C100	P2	700	300	200	28	

Tabla 4. Combinaciones fabricadas de gránulos

Sobre los gránulos fabricados se determinó su granulometría, realizando además termogravimetrías TG/DTG, densidad aparente (eliminando previamente gránulos > 20 mm), densidad de las partículas, absorción de agua y resistencia al aplastamiento, tomando para esto último 40 gránulos de 14 a 18 mm de diámetro de cada combinación (la fracción más abundante y en el número máximo disponible), y determinando la resistencia mecánica como un valor medio de los 40 ensayos, dividiendo las cargas por las áreas del gránulo en la sección de diámetro máximo.

Análisis de resultados y conclusiones

De la investigación realizada contenida en este artículo, se desprenden como más relevantes las siguientes consideraciones:

- Los gránulos producidos, presentaron formas fundamentalmente esféricas, obteniendo en todas las combinaciones curvas granulométricas con >95 % de tamaños de gránulos en el rango de 3,15/25 mm (ver *Fotografía 1*).
- En los ensayos termogravimétricos se identificaron claramente tres zonas características de descomposición de los productos cementantes generados en los gránulos, correspondientes a los procesos de deshidratación (entre 50° C y 200° C), deshidroxilación (entre los 250° C y 500° C) y de descarbonatación, con un pico máximo situado en los 650° C (ver *Figura 11*). Los resultados de las pruebas TG/DTG mostraron algunas tendencias interesantes entre las muestras, resaltando las diferencias de composición entre el tipo de SRW, la dosis de cementante, la atmósfera de curado y el tiempo de curado. Manteniendo constantes las demás variables, las combinaciones P2 mostraron en general menores pérdidas de masa relacionadas con los procesos de deshidratación, deshidroxilación y descarbonatación en comparación con P1. Esta diferencia se relacionó con el menor contenido de MgO en el P2 (41,11 %, frente al 76,13 % del P1), manteniendo P1 cierta reactividad y capacidad de hidratación para generar geles cementantes que se carbonatan en presencia de CO₂. No se observó un incremento significativo en el grado de hidratación entre 7 y 28 días, indicando una rápida formación de los geles cementantes a partir de MgO. Se observó también una relación directa entre el contenido de CO₂ de la atmósfera de curado y el grado de hidratación observado, incrementándose con la concentración de CO₂. Este dato contradice los resultados de otras investigaciones como los de Unluer y Al-Tabbaa (2015) quienes observaron cómo el CO₂ de la atmósfera de curado consume el MgO para carbonatación, no dejándolo disponible para la activación del GGBS.

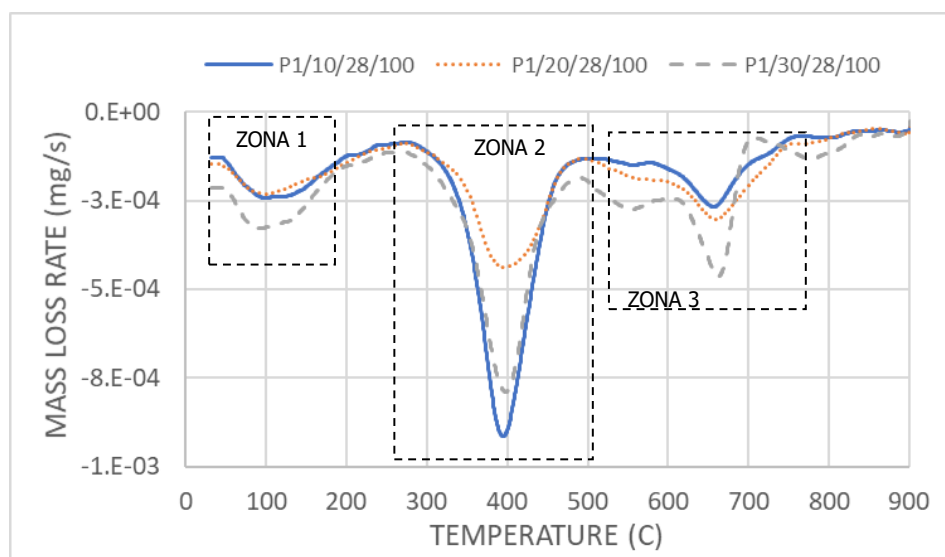


Figura 11. Curvas de descomposición DTG del P1

- Todas las combinaciones alcanzaron valores relativamente bajos de densidad de partículas y densidad aparente en comparación con los agregados naturales (ver Figuras 12 a 15). Las densidades aparentes fueron ligeramente superiores al valor de 1.200 kg/m³ que se establece para ser considerados áridos ligeros según la EN 13055. Las combinaciones P2 mostraron densidades de partículas y densidades aparentes más altas en comparación con las P1. Estas diferencias se atribuyeron a la granulometría más gruesa del P2 y a su mayor contenido de óxido de hierro. Varias de las combinaciones de gránulos fabricados con P1 (P1/10/28/A, P1/20/28/A, P1/20/28/C20, P1/20/28/C100 y P1/30/28/A) cumplieron con el requisito de densidad de partículas inferior a 2.000 kg/m³ establecido en la norma EN 13055-1 para ser considerados áridos ligeros para hormigón, mortero y lechadas.

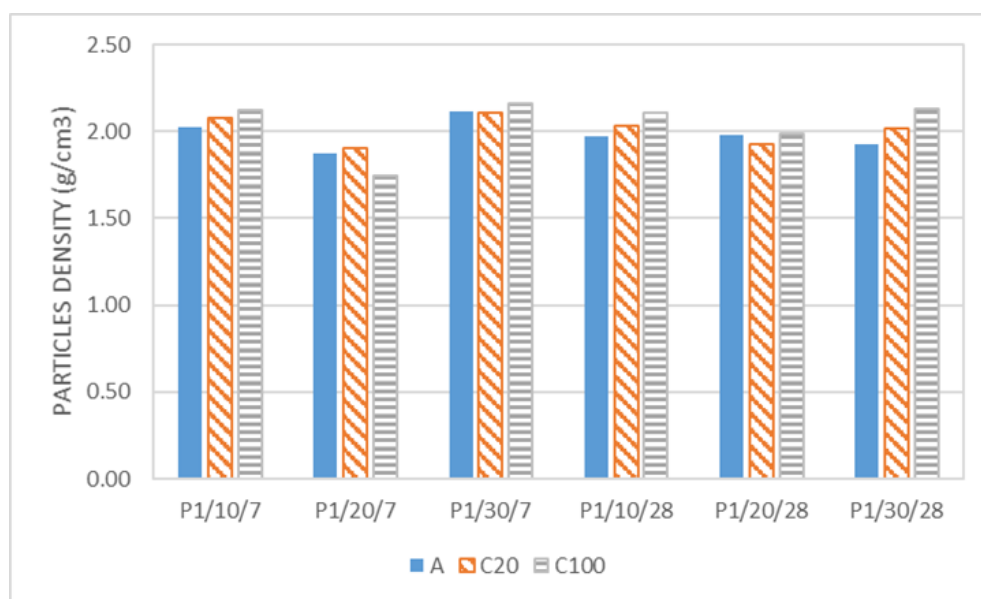


Figura 12. Densidad de las partículas de P1 en los distintos ambientes de curado

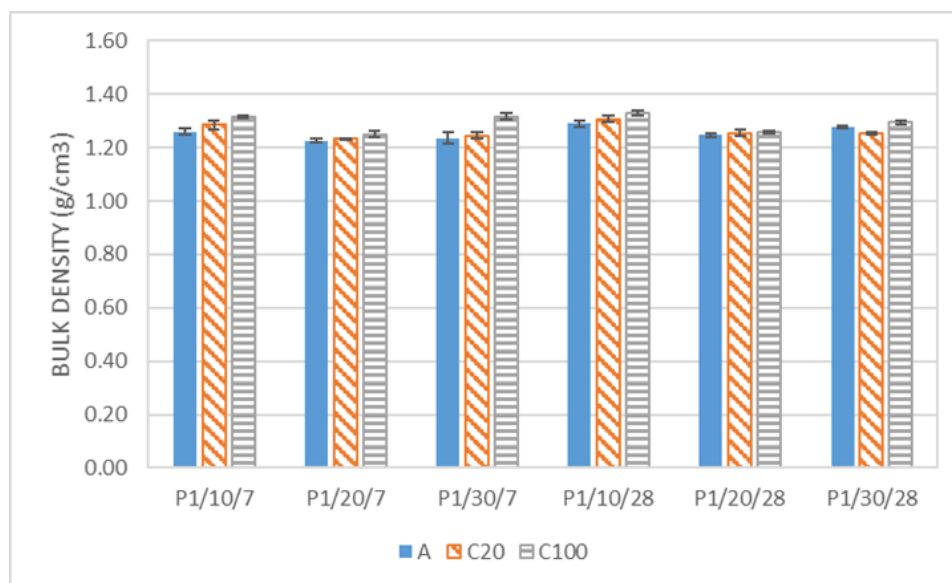


Figura 13. Densidad aparente de los gránulos P1 los distintos ambientes de curado

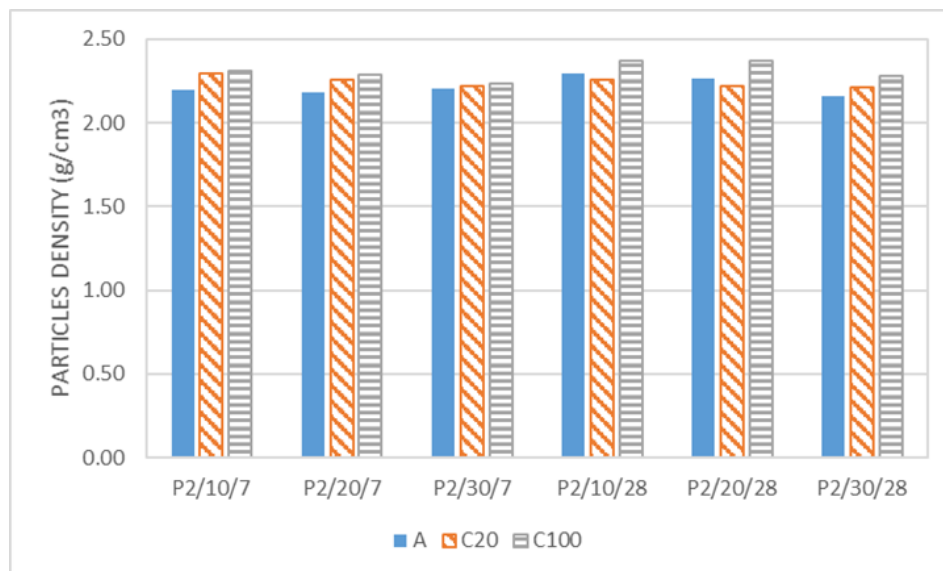


Figura 14. Densidad de las partículas de P2 en los distintos ambientes de curado

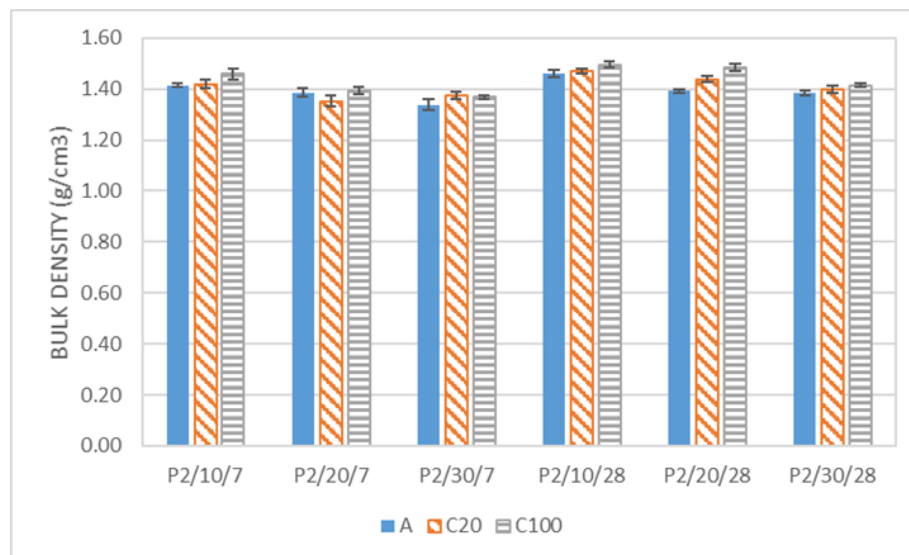


Figura 15. Densidad aparente de los gránulos P2 en los distintos ambientes de curado

- La carbonatación mostró un efecto beneficioso sobre la resistencia a la compresión de los gránulos, más claramente para las combinaciones de P2, principalmente cuando el curado se llevó a cabo en una atmósfera de 100 % de CO₂ (ver Figuras 16 y 17). Inesperadamente, las combinaciones P1 no mostraron ningún efecto directo entre la resistencia a la compresión y el contenido de aglutinante en cualquier edad o condición de curado. Así, por ejemplo, las combinaciones P1/10/28/20, P1/20/28/20 y P1/30/28/20 alcanzaron respectivamente resistencias a la compresión medias de 3,04 MPa, 1,34 MPa y 2,97 MPa. Lo mismo se observó en relación con el tiempo de curado, sin patrones claros de aumento de las resistencias a la compresión de 7 a 28 días. Entre las combinaciones P1, las mejores resistencias a la compresión las consiguieron las combinaciones P1/30/7/100, con 5,92 MPa, P1/30/28/100, con 5,37 MPa y P1/10/28/100, con 4,48 MPa. A pesar de las incertidumbres de los resultados, parece producirse una disminución de la resistencia a la compresión entre los 7 y 28 días de edad en las muestras

P1 curadas en una atmósfera con 100 % de CO₂. El descenso podría relacionarse con la formación de carbonatos de magnesio con una estructura relativamente débil o a la formación de minerales expansivos que dificultan la resistencia de los gránulos (Kim et al., 2019). Las muestras P2 mostraron tendencias de comportamiento general más claras. Las resistencias a la compresión aumentaron a medida que lo hizo el contenido de aglutinante. Para el mismo contenido de aglutinante, a la misma edad de curado, la resistencia a la compresión aumentó a medida que lo hizo la concentración de CO₂. De 7 a 28 días, las resistencias a la compresión de las muestras curadas al aire se mantuvieron estables, mientras que para los gránulos curados en atmósfera de CO₂ las resistencias a la compresión aumentaron, principalmente para las muestras curadas en una atmósfera de 100 % CO₂. Esto demostró el efecto beneficioso de la carbonatación de los gránulos para el desarrollo de su resistencia mecánica.

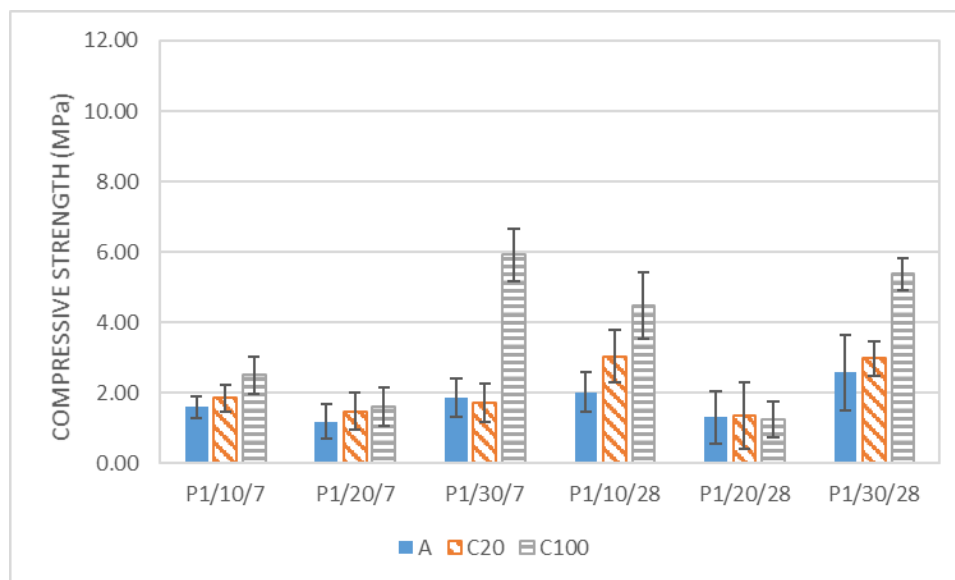


Figura 16. Representación de la resistencia a compresión de los gránulos P1

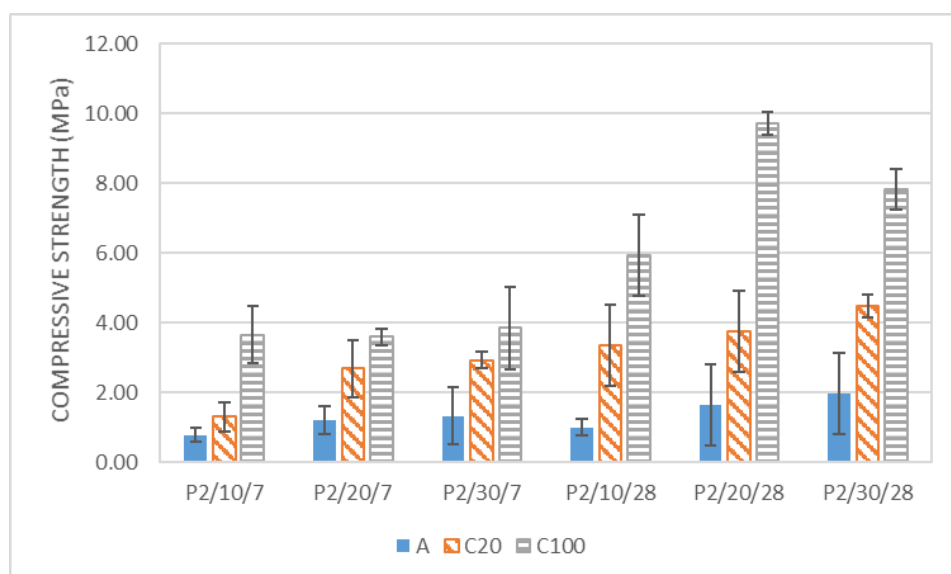


Figura 17. Representación de la resistencia a compresión de los gránulos P2

- La investigación empírica realizada demostró la efectividad de las condiciones de curado con CO₂ para la formación de geles cementantes y para el aumento del grado de carbonatación de los gránulos, contribuyendo a la reducción de la absorción de agua y al aumento de la resistencia a la compresión de los gránulos. Aunque los efectos beneficiosos del curado en atmósferas de CO₂ se observaron en las combinaciones de ambos SRW, su intensidad fue diferente en función de sus diferencias de composición y reactividad. Esto resalta la complejidad de los procesos que se superponen en el desarrollo de resistencia de los gránulos, como la cementación y la carbonatación.
- Volvió a demostrarse la capacidad cementante de la mezcla GGBS+PC8, ampliando las posibilidades de empleo de este cementante hidráulico.

5.2.- CAMPAÑA EXPERIMENTAL FASE 2: ARTÍCULO 3

ARTÍCULO 3: Estabilización de un suelo arcilloso utilizando GGBS y material cementante procedente de refractarios agotados

Introducción

En este artículo se ha evaluado la capacidad de tres residuos DMRR con distintos contenidos de magnesio procedentes de material refractario agotado, uno de dolomita y dos de magnesia, como aditivos estabilizadores de un suelo arcilloso mediante su uso directo y en combinación con GGBS.

Para esta investigación se ha llevado a cabo una campaña de ensayos de laboratorio, determinando resistencias a compresión simple de probetas cilíndricas de suelo aditivado y compactado, variaciones de plasticidad, variaciones de pH y capacidad de hinchamiento.

Materiales empleados

El suelo utilizado en esta investigación fue una muestra de arcilla recogida en el municipio de Pamplona (España). Este suelo arcilloso es el resultado de la meteorización in situ del sustrato rocoso local, constituido por margas grisáceas terciarias de estructura masiva. Se extrajo en total una tonelada de arcilla que, tras su secado al aire y homogeneización, se trituró y tamizó hasta tamaños de partículas de suelo por debajo de 2 mm.

Como estabilizantes del suelo, en este trabajo se emplearon tres tipos de DMRR: dos residuos refractarios de magnesia llamados P2B y P2-12 respectivamente, y un desecho refractario de dolomita llamado cal dolomítica (doloma lime, DL). Ambos residuos P2 se generan en la demolición del recubrimiento interior de cubas para la fundición del acero. El P2B es resultado de la denominación del material recuperado de la parte exterior de la cubeta refractaria, que está en contacto con el metal fundido y la escoria. Este hecho modifica su composición química y sinteriza el material refractario. El P2-12 es la parte interna del refractario de magnesia agotado. Dado que este material no está en contacto con el metal fundido ni con la escoria, mantiene una composición

química cercana a la del refractario crudo. DL está formado por los residuos refractarios agotados de hornos de cuchara. Muestra contenidos más altos de CaO y SO₃ que los desechos P2 debido a su contacto directo con la escoria de la cuchara. Las muestras de DMRR consideradas en esta investigación se molieron para reducir su granulometría y aumentar su superficie específica.

Coordenadas de toma de muestra		
X: 612.110 Y: 4.740.296 (UTM 30 ETRS89)		
Propiedades mecánicas del suelo		Propiedades químicas del suelo
Límites de Atterberg (UNE 17892-12):		Materia orgánica (UNE 103204): 0,32%
Límite Líquido: 38,4%		Sulfatos solubles (EN 1744-1): 0,05%
Límite Plástico: 22,8%		pH en agua: 7,88
Índice de Plasticidad: 15,6%		Mineralogía (difracción RX):
Proctor Normal (UNE 103500):		Calcita
Densidad máxima: 1,76 g/cm ³		Cuarzo
Humedad óptima: 18,5%		Haloisita
		Albita
Clasificación SUCS: CL		Composición química (fluorescencia RX):
Resistencia a compresión simple (UNE 17892-7):		Elemento: %
Antes de soaking: 0,619 MPa		Ca 50,41
Después de soaking: 0,000 MPa		Si 23,92
Hinchamiento libre (UNE 103601): 0,5%		Al 10,81
		Fe 7,78
		K 3,39
Índice CBR (UNE 103502): 2,44		Mg 1,92
		S 0,09
Color (basado en Tabla de Color Munsell):		
10YR 7/4		



Tabla 5. Características del suelo arcilloso empleado

El GGBS empleado fue suministrado por Heidelberg Cement Group (Reino Unido).

La proporción empleada de aditivo o combinaciones de aditivos, frente a suelo fue en todos los casos de un 5% en peso.

Composición química (Fluorescencia RX)				
%	P2B	P2-12	DL	GGBS
SiO ₂	12,45	10,53	12,38	32,18
CaO	10,89	9,8	29,37	43,94
Fe ₂ O ₃	12,13	3,31	2,54	0,33
Al ₂ O ₃	6,51	5,32	5,53	10,4
SO ₃	0,36	0,32	1,17	2
Cr ₂ O ₃	0,42	0,1	0,08	-
P ₂ O ₅	0,11	0,06	0,13	-
MnO	0,26	-	0	-
MgO	53,75	63,55	42,88	0,25
Reactividad				
Pérdida al fuego 1050 °C	6,02	4,26	5,91	0,46
Cal libre (%)	0,6	0,71	3,69	0,28
Reactividad (min)	>240 min	>240 min	>240 min	>480 min
pH en agua	11,62	11,73	12,07	9,54

Tabla 6. Composición química y parámetros de reactividad de los componentes empleados como cementantes

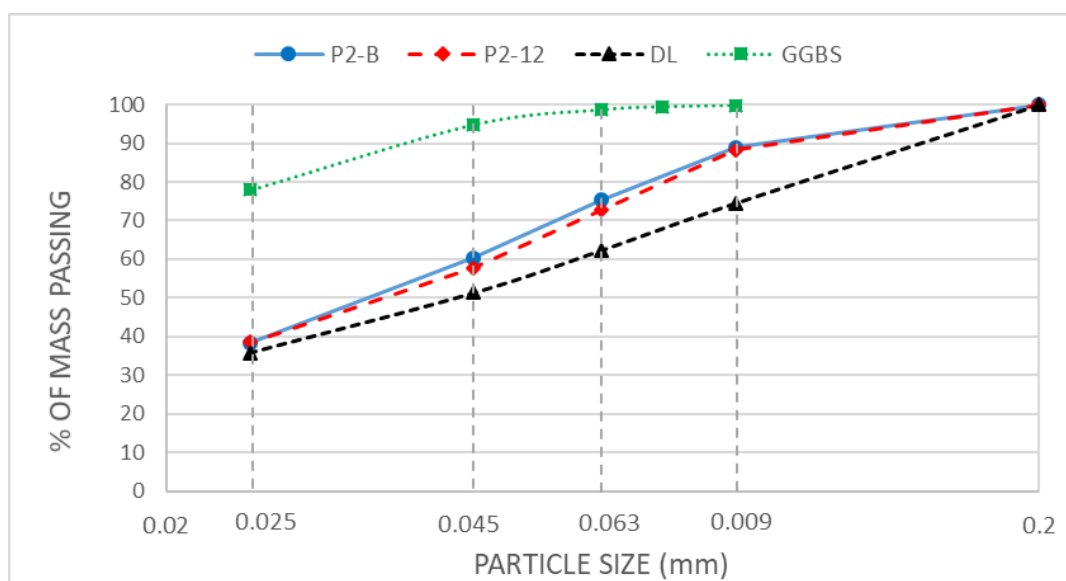


Figura 18. Curvas granulométricas de los componentes empleados como cementantes

Tipos de muestras analizadas y métodos

Para los ensayos de laboratorio se fabricaron muestras mezclando la tierra seca y los aditivos en una mezcladora de laboratorio durante 5 minutos. Después de eso, se añadió lentamente agua correspondiente a la humedad óptima del suelo, de acuerdo con el ensayo Proctor Normal (SP). Se realizó una mezcla adicional durante 5 minutos para garantizar una homogeneización completa del suelo, los aditivos y el agua. Una vez verificada visualmente la calidad de cada mezcla, se recogieron muestras para realizar pruebas de pH y límites de Atterberg.

Con las mezclas preparadas se fabricaron probetas cilíndricas de 65 mm de diámetro, (tres por cada combinación, edad de rotura y condiciones de ensayo de absorción), compactándolas en

moldes metálicos mediante una prensa hidráulica y aplicando 1,5 MPa. Esta presión fue la requerida para obtener la densidad máxima según el ensayo Proctor Normal. Una vez compactadas, las muestras se desmoldaron inmediatamente y se envolvieron en lámina de polietileno para evitar la deshidratación, manteniéndose hasta las edades de rotura (7, 28, 56 y 90 días) en una cámara húmeda a 20 °C y 100% de humedad relativa.

Los ensayos de compresión simple a las edades de 56 y 90 días, se llevaron a cabo sobre dos conjuntos de muestras: uno sin ningún acondicionamiento tras las edades de curado y otro después de 24 horas de acondicionamiento por humedad, tras un proceso asimilable a una absorción de agua por capilaridad, según se define en Li et al. (2020). Tras las roturas, se determinó el pH de las muestras sin acondicionamiento por humedad. A los 28 y 90 días, fragmentos de las muestras ensayadas a compresión simple, se trituraron y se secaron durante una semana a 40°C en un desecador con gel de sílice y un absorbente de CO₂. Este proceso se llevó a cabo para detener por completo las reacciones de cementación, y realizar sobre ellas difracción de rayos X (XRD).

Se realizó además prueba de expansividad mediante hinchamiento libre en edómetro, en condiciones de densidad y humedad Proctor Normal, para valorar cualquier efecto expansivo de las muestras de suelo tratadas.

En la Tabla 7 se muestran las combinaciones ensayadas.

COMBINACION	CÓDIGO	SUELO	P2-B	P2-12	DL	GGBS
SOIL	SOIL	100				
SOIL + P2B	P2-B (100/0)	95	5			
SOIL + P2-12	P2-12 (100/0)	95		5		
SOIL + DL	DL (100/0)	95			5	
SOIL + GGBS	GGBS	95				5
SOIL + P2B + GGBS (30/70)	P2-B (30/70)	95	1,5			3,5
SOIL + P2B + GGBS (50/50)	P2-B (50/50)	95	2,5			2,5
SOIL + P2B + GGBS (70/30)	P2-B (70/30)	95	3,5			1,5
SOIL + P2-12 + GGBS (30/70)	P2-12 (30/70)	95		1,5		3,5
SOIL + P2-12 + GGBS (50/50)	P2-12 (50/50)	95		2,5		2,5
SOIL + P2-12 + GGBS (70/30)	P2-12 (70/30)	95		3,5		1,5
SOIL + DL + GGBS (30/70)	DL (30/70)	95			1,5	3,5
SOIL + DL + GGBS (50/50)	DL (50/50)	95			2,5	2,5
SOIL + DL + GGBS (70/30)	DL (70/30)	95			3,5	1,5

Tabla 7. Distintas proporciones de las combinaciones ensayadas

Análisis de resultados y conclusiones

De la investigación realizada contenida en este artículo, se desprenden como más relevantes las siguientes consideraciones:

- Las muestras tratadas con P2B, P2-12 y GGBS, disminuyeron ligeramente su plasticidad, no observándose una diferencia apreciable cuando se trató el suelo con DL. Estas variaciones de plasticidad se atribuyeron a diferentes procesos físicos y químicos entre el suelo y los aditivos que pueden superponerse entre sí. Entre ellos se encuentran la modificación de la granulometría

del suelo por la adición de partículas de aditivo, la floculación del suelo o la ocurrencia de reacciones de hidratación cementante.

COMBINACIÓN	LL	PL	PI
SOIL	38,4	22,8	15,6
P2B (100/0)	34,2	20,0	14,2
P2-12 (100/0)	36,1	20,8	15,3
DL (100/0)	38,3	21,7	16,6
GGBS	32,8	19,9	12,9
P2B (30/70)	33,1	20,4	12,7
P2B (50/50)	33,1	19,4	13,7
P2B (70/30)	35,3	19,5	15,8
P2-12 (30/70)	34,1	20,3	13,8
P2-12 (50/50)	35,2	20,7	14,5
P2-12 (70/30)	35,8	20,0	15,8
DL (30/70)	37,2	22,1	15,1
DL (50/50)	38,0	22,0	16,0
DL (70/30)	38,5	23,0	15,5

Tabla 8. Valores de plasticidad de las combinaciones ensayadas: Límite Líquido (LL), Límite Plástico (PL) e Índice de Plasticidad (PI)

- Se observaron incrementos de pH en las combinaciones que contenían P2B, P2-12 y GGBS desde el día 7 hasta el día 28 (Figuras 19 a 21). A partir de esa edad, el pH disminuyó ligeramente hasta los 90 días. Estos comportamientos observados son consecuencia del contenido de CaO y MgO en los aditivos, así como de los mecanismos de hidratación, disolución y precipitación de las reacciones puzolánicas (Z. Li et al., 2014; Zheng et al., 2019). La lentitud del proceso y los pequeños aumentos de pH demuestran una baja disponibilidad de CaO y MgO libres. Por otro lado, las combinaciones con DL mostraron ligeras disminuciones de pH durante todo el tiempo de curado, alcanzando el valor más alto de la investigación de laboratorio, con 11,15. Esto evidenció que este aditivo contenía cantidades apreciables de cal libre disponible que se hidrataba antes de los 7 días. Estos resultados concuerdan con los de otros autores que observaron que con MgO y CaO libre, los aumentos de pH ocurrieron entre 0 y 14 días (Jin & Al-Tabbaa, 2013; T. Zhang et al., 2011; Zheng et al., 2019). El entorno alcalino es necesario para romper los enlaces covalentes Si-O y Al-O en las partículas de GGBS y arcilla. No hay un consenso sobre el pH necesario para este proceso de activación, considerando que diferentes autores afirman que los valores de pH requeridos están en el rango de 11–12 (Zheng et al., 2019). Posteriormente, los iones Ca²⁺ y Mg²⁺ reaccionan con Si-O ó Al-O para formar geles cementantes de silicato de calcio hidratado (CSH), aluminato de calcio hidratado (CAH), silicato de magnesio hidratado (MSH) y aluminato de magnesio hidratado (MAH). Este proceso consume OH⁻, lo que produce la disminución del pH observada en las muestras (Z. Li et al., 2014).

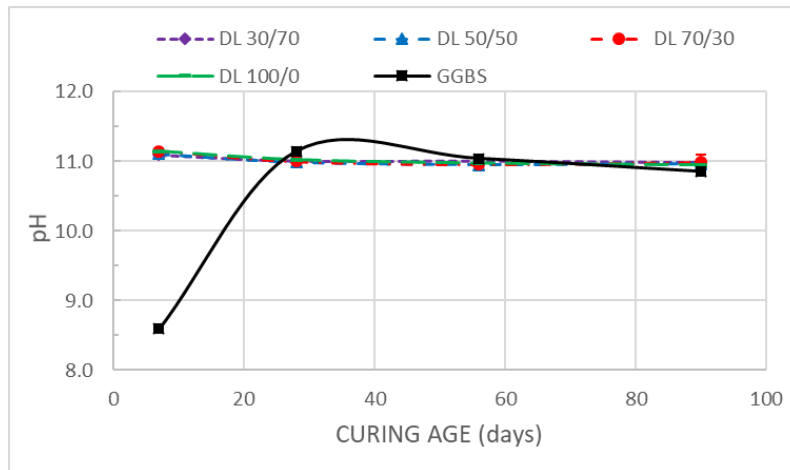


Figura 19. Valores de pH a lo largo del tiempo de curado para combinaciones DL

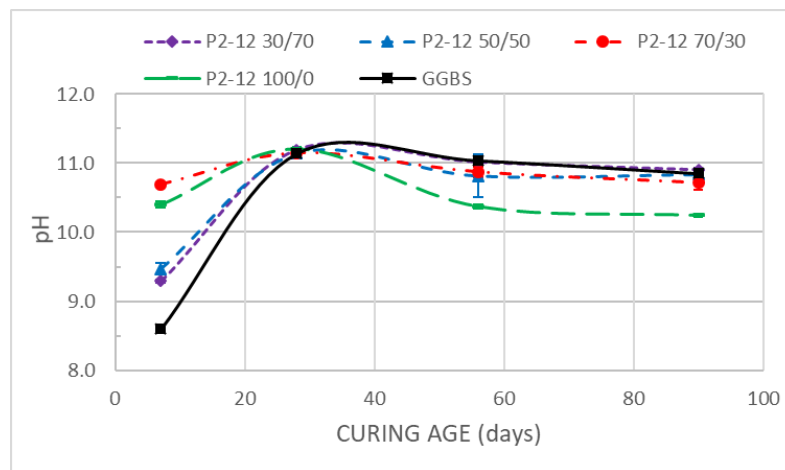


Figura 20. Valores de pH a lo largo del tiempo de curado para combinaciones P2-12

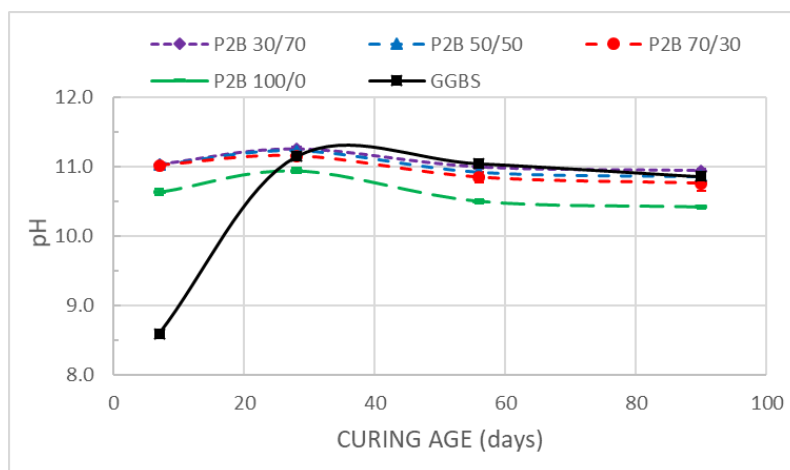


Figura 21. Valores de pH a lo largo del tiempo de curado para combinaciones P2B

- Respecto a las resistencias a compresión, para todas las combinaciones se observó una correlación directa entre el tiempo de curado y el incremento en las resistencias (Figuras 22 a 25). Esto demostró que los aditivos utilizados tenían una baja reactividad que se

desarrollaba con el paso del tiempo. Considerando las combinaciones de los aditivos no mezclados, GGBS mostró una mejor capacidad cementante en comparación con P2B (100/0) y P2-12 (100/0), pero menor que DL (100/0), que alcanzó los valores más altos de UCS en todas las edades de curado. Este hecho se atribuyó a la mayor riqueza de CaO reactivo en el GGBS y de CaO y MgO reactivos en el DL. Estos óxidos de los aditivos actuaron como activadores de las reacciones puzolánicas y se combinaron con su propio silicio y aluminio, o con los aluminosilicatos de la arcilla, para formar compuestos cementantes. La cantidad y reactividad diferentes de estos óxidos presentes en los aditivos justifican las diferencias de UCS entre las combinaciones no mezcladas. En las distintas combinaciones de GGBS+aditivos, las mayores resistencias se obtuvieron con dosificaciones altas de GGBS frente al otro aditivo, considerándose como óptimo la sustitución de GGBS por el otro aditivo en el rango del 30% al 50%. Las combinaciones GGBS + DL obtuvieron los valores más elevados de resistencia a compresión, demostrando su mayor reactividad y su capacidad para formar compuestos cementantes con los aluminosilicatos del suelo y su capacidad para activar el GGBS.

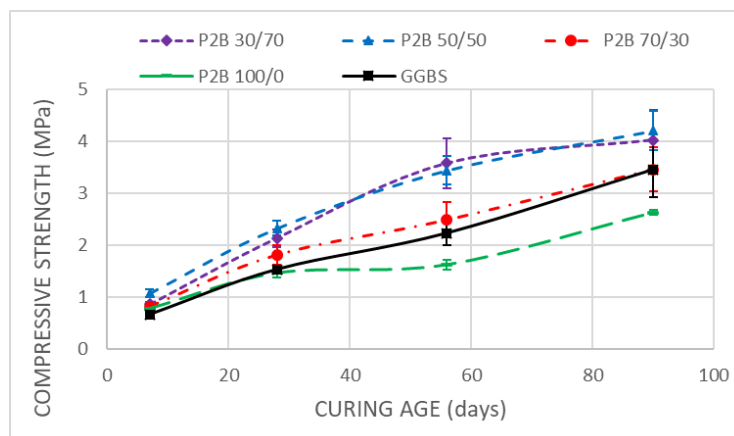


Figura 22. Evolución con el tiempo de la resistencia a compresión simple de las combinaciones P2B

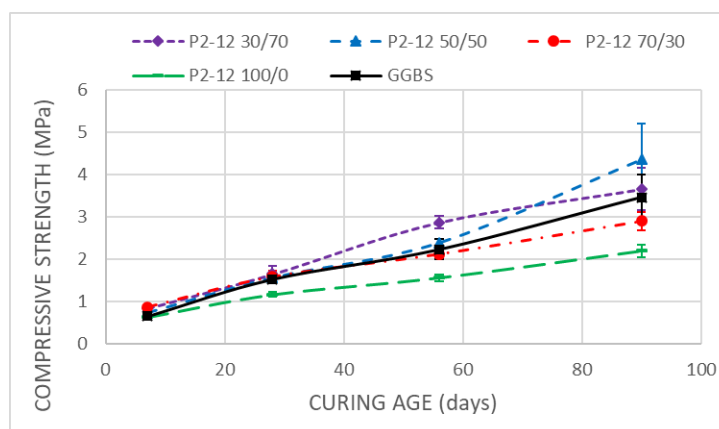


Figura 23. Evolución con el tiempo de la resistencia a compresión simple de las combinaciones P2-12

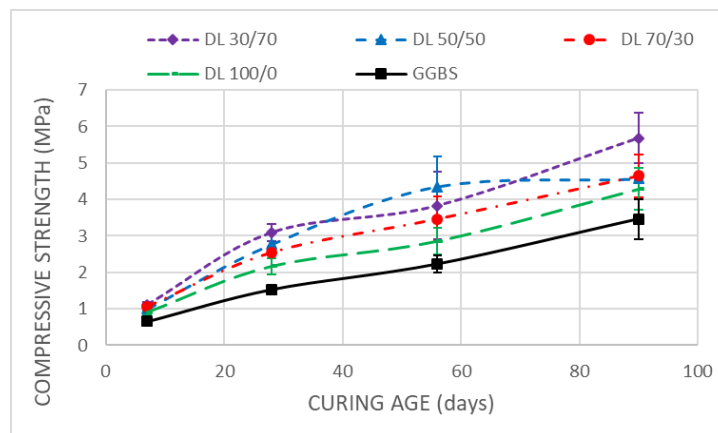


Figura 24. Evolución con el tiempo de la resistencia a compresión simple de las combinaciones DL

- Respecto a las probetas ensayadas tras el acondicionamiento por humedad, todas las combinaciones mostraron pérdidas de resistencia a los 56 y a los 90 días, en un rango del 68,70% al 94,41%. Estos resultados demostraron que, como era de esperar, el agua desempeña un papel significativo en la pérdida de resistencia de los suelos estabilizados.
- Si bien el suelo arcilloso empleado en esta investigación no presentaba un elevado índice de hinchamiento de libre (un 0,48%, obtenido a los tres días de ensayo), con el empleo de los aditivos se han obtenido algunos resultados reseñables que se exponen a continuación. Con excepción de la combinación DL (70/30), el resto rebajaron la escasa expansividad natural del suelo, alcanzando cada una de ellas su valor máximo antes de 3 días de pruebas, manteniéndose estable después. Esto demostró la inexistencia de posibles casos de hinchamiento retardado debido a la hidratación de los constituyentes de los aditivos. DL (70/30) aumentó ligeramente el hinchamiento natural del suelo, necesitándose 9 días de pruebas para alcanzar su valor máximo. Este aumento no se produjo en las combinaciones DL (30/70) y DL (50/50) lo que indica de nuevo que proporciones GGBS+aditivo son cercanas a la proporción óptima del cementante. Si bien en la literatura se indica la existencia de procesos de hidratación retardada en aglutinantes binarios de MgO-GGBS por Li et al. (2020), considerando los bajos valores de hinchamiento de las combinaciones de DL y el bajo aumento de hinchamiento (0,1%) entre los días 6 y 9, este hecho se atribuyó a incertidumbres experimentales.

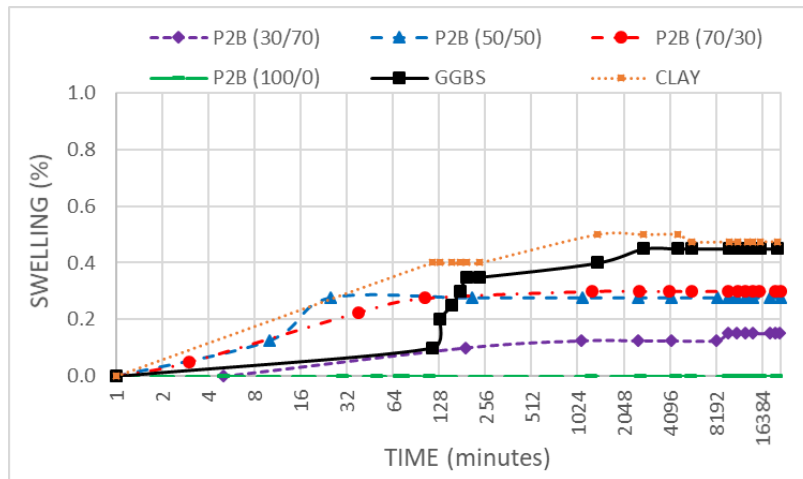


Figura 25. Evolución con el tiempo del hinchamiento libre en combinaciones P2B

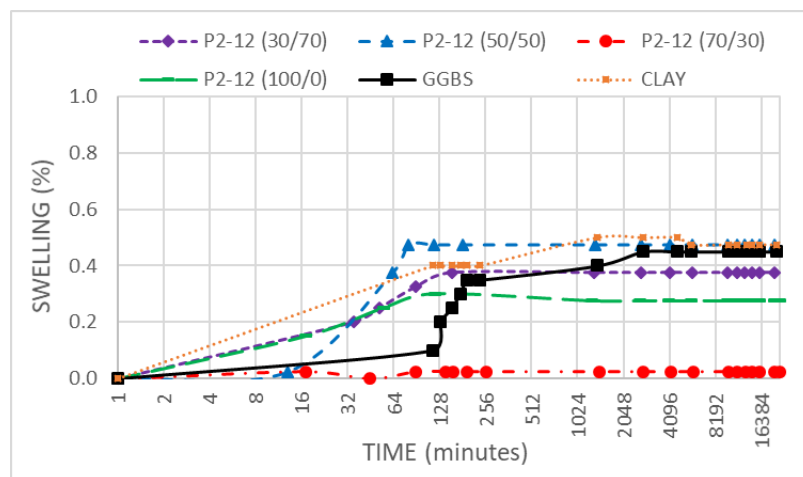


Figura 26. Evolución con el tiempo del hinchamiento libre en combinaciones P2-12

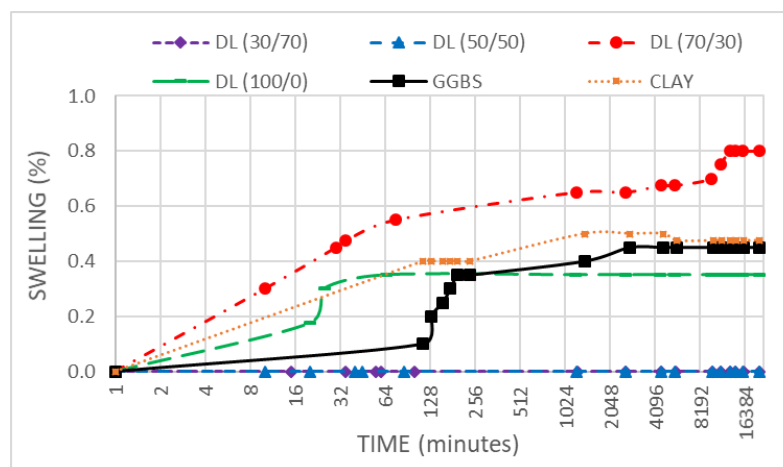


Figura 27. Evolución con el tiempo del hinchamiento libre en combinaciones DL

- En las pruebas de DRX realizadas sobre todas las combinaciones de suelo tratado (a las edades de 28 y 90 días), se observó la existencia de picos en las muestras estabilizadas que

no aparecen en el difractograma del suelo natural, lo que puede atribuirse bien a las diferentes composiciones de los aditivos empleados o a cambios químicos en las muestras debido al proceso de cementación. La intensidad de los picos estaría relacionada con las dosis de aditivos o con la formación o destrucción de minerales. En conjunto, a la edad de 28 y 90 días, las diferencias de mineralogías fueron pequeñas, mostrando en todos los casos las fases cristalinas del suelo natural. No se observaron minerales de DMRR o GGBS debido al bajo grado de cristalinidad de estos materiales, la baja dosis considerada y la superposición de sus picos con los de los minerales del suelo (Gomes & de Oliveira, 2018; Yi et al., 2015). El único producto de hidratación observado fue un pico a 2 theta (35°) que se atribuyó a la formación de geles MSH según la referencia (H. Zhang et al., 2018).

5.3.- CAMPAÑA EXPERIMENTAL FASE 3: ARTÍCULOS 4 Y 5

5.3.1.- ARTÍCULO 4: *Estabilización de suelos con sulfato mediante cementantes con base de magnesio, para la construcción de explanadas de carreteras*

Introducción

En este artículo se ha evaluado la capacidad de aditivos a base de óxido de magnesio para estabilizar un suelo con alto contenido en yeso y baja capacidad portante, con el fin de alcanzar los requisitos para la formación de una explanada para obra vial. Los aditivos considerados en esta investigación estuvieron compuestos por tres productos y subproductos reactivos de MgO, con y sin la adición de GGBS. El empleo de estos aditivos se comparó con dos cementos comunes tipo Portland y una cal aérea como estabilizadores del suelo, en una investigación de laboratorio y una prueba de campo.

Materiales empleados

El suelo utilizado en esta investigación fue una muestra de margas yesíferas recogidas en el municipio de Mañeru (España). Este suelo margoso se clasifica según el Sistema Internacional de Clasificación de Suelos (USCS) como CL-ML. Según la Instrucción de Carreteras de España (Ministerio de Fomento, 2002), este suelo se clasifica como 'suelo marginal'. Dicha clasificación limita el uso de este material a las cimentaciones y el núcleo de terraplenes y lo excluye para la construcción de la parte superior de terraplenes y subbases en la construcción de carreteras.

SUELO	Marga yesífera
Origen	Mañeru (España)
Coordenadas WGS84	42° 39' 49.89" N 1° 51' 23.89" W
Límites de Atterberg:	
LL (UNE 103103)	21,0
PL (UNE 103104)	15,0
PI	6,0
Clasificación USCS	CL-ML
Proctor Normal (EN 13286-2)	
Densidad máxima (g/cm ³)	1,87
Humedad óptima (%)	11,4
Índice CBR (UNE 103502)	8
Hinchamiento libre (UNE 103601)	2,30%
Materia orgánica (UNE 103204)	0,40%
Sulfatos solubles (EN 1744-1)	20,64%
Granulometría (EN 933-1)	
Tamiz (mm)	% pasa
4	100
1	100
0,63	92
0,4	84
0,25	76
0,08	60,6
Mineralogía (Difracción RX)	Yeso Calcita Cuarzo Dolomita Mica

Tabla 9. Características del suelo con alto contenido en sulfatos empleado en la investigación

En cuanto a los aditivos utilizados para la estabilización, se emplearon por una parte cementantes comerciales usados habitualmente como estabilizadores de suelos (utilizándose además como cementantes de referencia); y por otra, tres aditivos de MgO reactivos procedentes del proceso de la fabricación de material refractario a partir de la calcinación de magnesita. Los aditivos comerciales fueron dos cementos tipo Portland denominados CEM I 52.5 N (PC) y CEM I 52.5 N SR (RS-PC) y una cal hidratada tipo CL-90 (HL). Los aditivos con base de magnesio fueron el producto comercial MCB100 y los subproductos PC-8 y Sulfamag de MAGNA.

Composición química (%)	Aditivos con base Ca			Aditivos con base Mg			
	CEM I 52.5	CEM I 52.5 SR	CL-90-S	MCB 100	PC-8	SULFAMAG	GGBS
SiO ₂	9,17	9,56	0,45	3,41	2,8	1,41	32,18
CaO	76,32	74,43	97,83	3,79	9,1	32,9	43,94
Fe ₂ O ₃	5,63	7,44	0,18	2,9	2,34	1,11	0,33
Al ₂ O ₃	2,96	2,49	0,02	0,82	0,57	0,56	10,4
SO ₃	2,07	2,45	0,43	0,21	6,27	19,71	2
MgO	1,08	1,18	0,72	82,26	59,67	25,06	9,05
Pérdida al fuego 1.050° C	4,97	4,36	25,32	6,61	19,25	19,25	0,91
Reactividad ácido cítrico (min)	>600	>600	4	2	29	1119	>600
pH en agua (UNE-ISO 10390)	11,88	12,31	12,47	10,88	10,66	12,63	9,82
Cal libre (%)	3,67	3,84		1,04	0,81	13,08	0,28

Tabla 10. Características químicas de los aditivos empleados

Tipos de muestras analizadas y métodos

Para la investigación de laboratorio se tomó una tonelada del suelo yesífero, siendo triturada hasta un tamaño máximo de un mm y homogeneizada. Con esta muestra se llevaron a cabo en laboratorio ensayos de compresión simple y análisis de lixiviados sobre las diferentes combinaciones de suelo estabilizado utilizando dosificaciones de cementante del 5% y 10% en peso. Se prepararon para ello probetas cilíndricas de 65 mm de diámetro y 75 mm de alto, compactadas en moldes metálicos hasta alcanzar densidades correspondientes a la del Proctor Normal. Las probetas producidas fueron inmediatamente desmoldadas y cubiertas con lámina de polietileno para evitar su deshidratación, almacenándose hasta la edad de ensayo (7, 14, 28, 56 y 90 días) en una cámara húmeda a 20 °C y 100% de humedad relativa. Sobre las probetas ensayadas a compresión a las edades de 28 y 90 días, se realizaron análisis de lixiviados junto a muestras del suelo natural y de los aditivos empleados (todos ellos por separado).

COMBINACIÓN	SUELO	Aditivo con base Ca			Aditivo con base Mg			
		CEM I 52.5	CEM I 52.5 SR	CL-90-S	MCB100	PC-8	SULFAMAG	GGBS
1	95	5						
2	90	10						
3	95		5					
4	90		10					
5	95			5				
6	90			10				
7	95				5			
8	90				10			
9	95					5		
10	90					10		
11	95						5	
12	90						10	
13	95			1				4
14	90			2				8
15	95					1		4
16	90					2		8
17	95				1			4
18	90				2			8
19	95						1	4
20	90						2	8

Tabla 11. Combinaciones consideradas para ensayo de compresión simple

Sobre las combinaciones con 5% de CEM I, CEM I SR, CL-90-S, PC-8, MCB100 y Sulfamag se realizaron ensayos de hinchamiento libre, sobre probetas compactadas en condiciones de Proctor Normal, extendiendo el ensayo hasta los 50 días de duración para observar posibles hinchamientos retardados por la formación de geles expansivos. Tras la finalización de los ensayos de hinchamiento, sobre estas muestras se realizó DRX para identificar posibles cambios mineralógicos y especialmente verificar la formación de etringita.

Por otro lado, se llevó a cabo la construcción de una zona de pruebas de campo para evaluar la capacidad de carga del material estabilizado. La prueba en el campo se realizó en la localidad Eugi (Navarra). Para ello, en primer lugar, se niveló y compactó el suelo in situ, y se marcaron las diferentes secciones o zonas de ensayo, de 4 × 5 metros. Se extendió y niveló el suelo yesífero para garantizar una capa homogénea de 25 cm. En cada sección, se esparcieron los aditivos y se mezclaron utilizando un rotavator, asegurándose de no contaminar las secciones adyacentes. Para esta prueba, se consideraron las combinaciones CEM I, CEM I SR, CL-90-S + GGBS, PC-8+GGBS, MCB100+GGBS y Sulfamag + GGBS al 5% y 10%. Una vez preparadas las diferentes mezclas de suelo y aditivos, se agregó el contenido óptimo de agua del ensayo SP mediante un camión cisterna y se mezcló nuevamente para garantizar la distribución correcta de la humedad en todo el espesor de la capa. El contenido de agua se verificó mediante un densímetro nuclear y un medidor de humedad. El suelo tratado se compactó mediante un compactador vibratorio de obra civil hasta alcanzar la densidad máxima SP. Después, la zona de pruebas de campo quedó expuesta a las

condiciones ambientales, realizándose ensayos de carga con placa en todas las secciones, para evaluar la capacidad de carga y deformabilidad del suelo, a una edad de 40 y de 140 días desde su estabilización.



Fotografía 2. Suelo yesífero extendido



Fotografía 3. Dosificación de cementantes en zona de pruebas



Fotografía 4. Mezclado de suelo y cementantes



Fotografía 5. Compactación de zona de pruebas



Fotografía 6. Imagen de la zona de pruebas de campo tras 40 días desde su estabilización

Análisis de resultados y conclusiones

De la investigación realizada en laboratorio, se desprenden como más relevantes las siguientes consideraciones:

- En los ensayos de resistencia a compresión simple se obtuvieron para todas las combinaciones incrementos de la resistencia a lo largo del tiempo (*Figuras 28 a 31*). En las combinaciones sin GGBS, los valores más elevados de resistencia se obtuvieron con el CEM 52.5 al 10%, alcanzando un valor de 17,5 MPa a 90 días. Este inesperado resultado podría deberse a la capacidad del $\text{Ca}(\text{OH})_2$ producido como subproducto de la hidratación del cemento para activar los óxidos de aluminio y silicio del suelo y generar compuestos cementantes adicionales. También resulta muy destacable que el tratamiento con un 5% de cal logró una resistencia a compresión simple de 12,2 MPa a los 90 días, superando el resultado obtenido con el CEM I SR. Esto demuestra la capacidad de la cal para activar el aluminio y el silicio de la matriz arcillosa del suelo para producir geles cementantes. Sin embargo, cuando se utilizó un 10% de cal, la resistencia disminuyó a 10,2 MPa a los 90 días, mostrando un exceso de dosificación (Seco, Ramírez, Miqueleiz, García, et al., 2011). Con el uso de los aditivos PC-8, MCB100 y Sulfamag (al 5% y 10%) la ganancia de resistencia fue muy inferior, alcanzando a 90 días resistencias entre 5 y 7 MPa, lo que demuestra que estos aditivos, por si solos, tienen una capacidad inferior a la cal para activar los óxidos en un suelo de baja reactividad. Inesperadamente, pero de acuerdo con los resultados obtenidos por Seco et al. (2017), no se observaron efectos adversos relacionados con la presencia de etringita en las muestras, a pesar del alto contenido de sulfato y calcio en muchas de las combinaciones. En cuanto a las combinaciones con GGBS, todas las muestras mostraron un aumento en la resistencia a la compresión para todas las combinaciones en todas las edades de curado y para ambas dosis, demostrando la reactividad del GGBS y la capacidad de la cal, PC-8, MCB100 y Sulfamag para activarlo. La mejor combinación de aditivos que contenía GGBS fue MCB100+GGBS, alcanzando a los 90 días los 18,1 MPa para las dosis 10%. PC-8, MCB100 y Sulfamag, combinados con GGBS y una dosis del 5%, lograron valores de resistencia que superaron los obtenidos por CEM I 52.5 después de 90 días. Estos valores demuestran la ventaja de los aditivos a base de MgO combinados con GGBS para la estabilización del suelo.

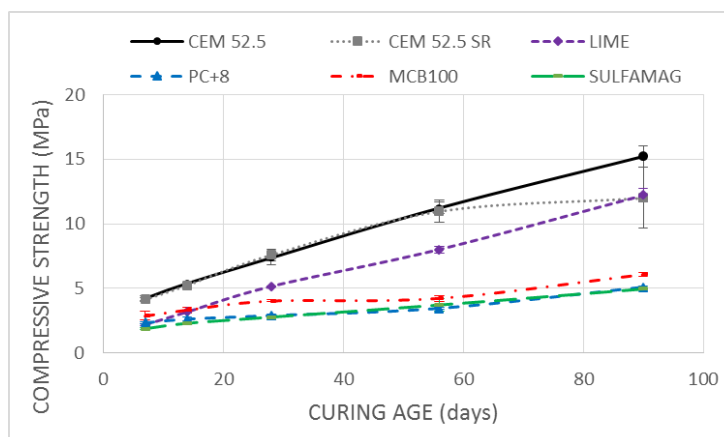


Figura 28. Evolución de las resistencias a compresión simple de muestras sin GGBS dosificadas al 5%

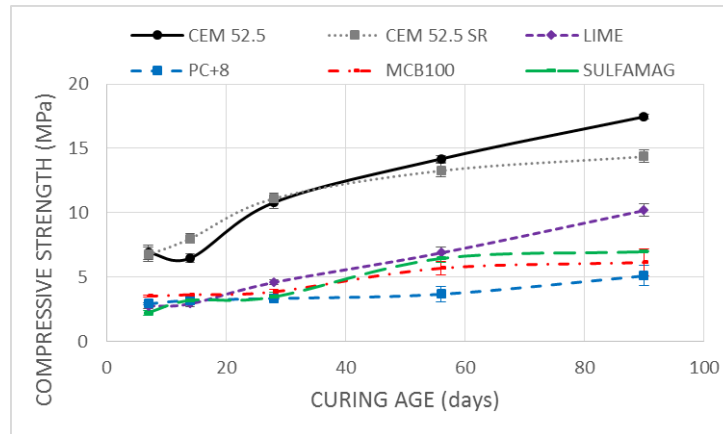


Figura 29. Evolución de las resistencias a compresión simple de muestras sin GGBS, dosificadas al 10%

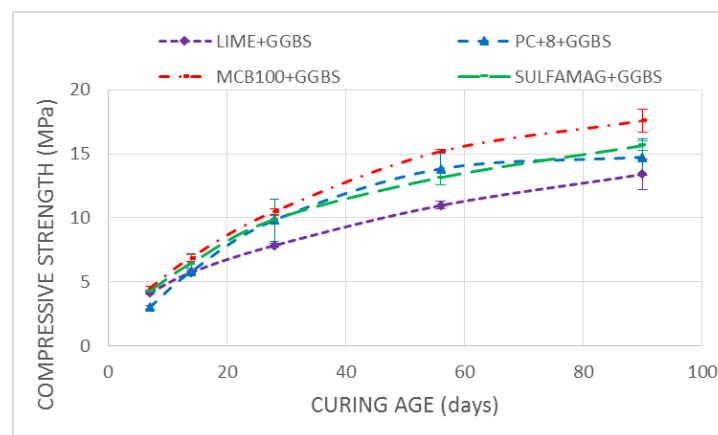


Figura 30. Evolución de las resistencias a compresión simple de muestras con GGBS, dosificadas al 5%

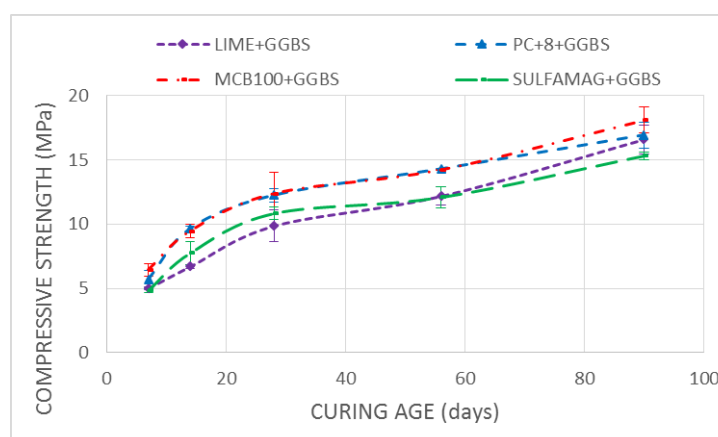


Figura 31. Evolución de las resistencias a compresión simple de muestras con GGBS dosificadas al 10%

- De los ensayos de hinchamiento libre en edómetro se extraen también importantes conclusiones (Figuras 32 y 33). Tras 24 horas, la combinación CEM I redujo el hinchamiento libre del suelo del 2,3% a 0,1%, siendo algo inferior la combinación CEM I SR, que la redujo al 0,5%. Esto demuestra un aparente efecto beneficioso a corto plazo de estos ligantes en

la disminución de la expansividad del suelo. Sin embargo, la hidratación y el fraguado del cemento Portland son procesos rápidos que retrasan la expansividad de la etringita, pero no la detienen por completo. Así, se observó cómo los suelos con CEM I SR superaron la expansión del suelo natural después de 20 días, alcanzando un hinchamiento del 5,1% a los 50 días. También la muestra con CEM I superó el hinchamiento del suelo natural después de 27 días, alcanzando el 3,3% a los 50 días. Estos resultados inesperados muestran una mayor capacidad de formación de etringita en el suelo tratado con cemento resistente a sulfatos en comparación con el convencional. La muestra CL-90-S alcanzó un hinchamiento del 5,3%, demostrando el efecto negativo del exceso de Ca sobre la expansión y la probable formación de compuestos expansivos. Después de 24 horas, MCB100 y Sulfamag mostraron valores de hinchamiento del 3,0% y 6,2%, respectivamente, que también se atribuyeron a la disponibilidad de Ca. PC-8 alcanzó una expansión del 1,8% que ligeramente disminuyó la expansión natural del suelo. La cal y Sulfamag mostraron un aumento del hinchamiento durante el período de 50 días, alcanzando respectivamente el 42,6% y 35%. Este comportamiento demuestra la formación de grandes cantidades de minerales de expansión hidratados en estas muestras, probablemente etringita. Estos valores de expansión contrastan con la aparente falta de daño en las probetas de compresión simple y los valores crecientes de resistencia a lo largo del tiempo de curado para ambas combinaciones. Estas diferencias se deben probablemente a la alta disponibilidad de agua en el edómetro en comparación con las probetas de compresión simple, lo que favorece la formación de etringita.

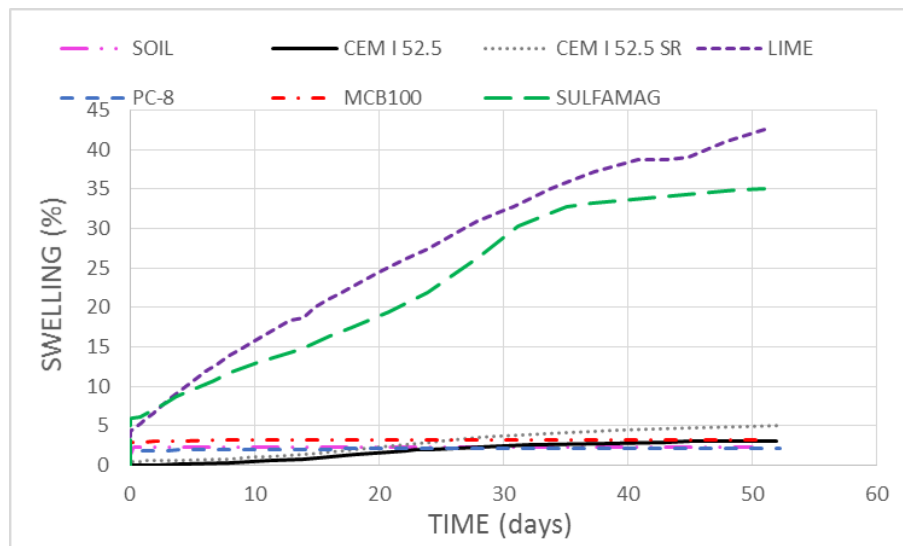


Figura 32. Evolución del hinchamiento libre de las distintas combinaciones (representando hasta un 45% de hinchamiento)

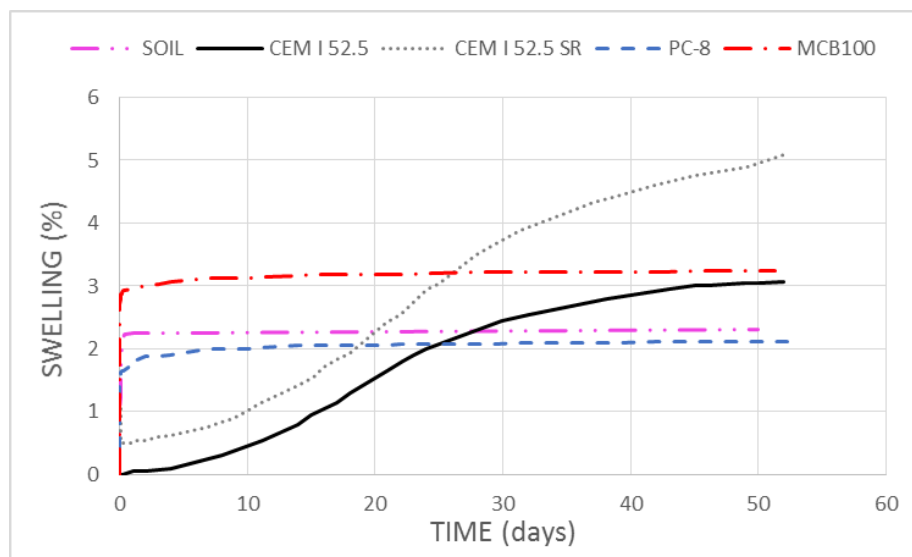


Figura 33. Evolución del hinchamiento libre de las distintas combinaciones (representando hasta un 6% de hinchamiento)

- En las difracciones de rayos X se identificó la presencia de etringita en las muestras de las combinaciones tratadas con CL-90-S y Sulfamag. Sin embargo, no se detectó su presencia en los difractogramas de las combinaciones CEM I y CEM I SR, donde también se esperaba su presencia. Este hecho, junto con el pequeño tamaño de los picos de etringita en los difractogramas de las muestras donde se observó este mineral, sugiere, como también lo sugieren Seco et al. (2017), que el tipo de etringita observada tendría una estructura cristalina baja, o más probablemente, que aparecería en pequeñas cantidades, lo que dificulta su identificación.
- Los valores de lixiviados obtenidos se compararon con parámetro de lixiviación considerados por las normativas de lixiviación españolas para clasificar un material como "inerte" según la clasificación Ministerio de Medio Ambiente de 2013 para residuos en vertederos. El suelo yesífero empleado en la prueba de campo superó la lixiviación de sulfatos clasificándose como "no peligroso". Después de 28 días, el suelo sin estabilizar y las combinaciones estabilizadas mantuvieron la lixiviación de la mayoría de los metales por debajo de los valores de referencia y solo CEM I SR superó la lixiviación de Cr. Se observó un aumento en la lixiviación de metales en las combinaciones estabilizadas con CEM I, CEM I SR y MCB100+GGBS después de 90 días. La estabilización tuvo un efecto beneficioso en la lixiviación de Ca y Mg, que disminuyó en comparación con el suelo natural en ambas edades de curado. Después de 28 días, CEM I aumentó la lixiviación de sulfatos de 1,626 mg/l a 1,801 mg/l, mientras que CEM I SR, PC-8+GGBS, MCB100+GGBS y Sulfamag + GGBS la redujeron. A los 90 días, todas las combinaciones redujeron la lixiviación de sulfatos observada a los 28 días. La estabilización de este suelo redujo la lixiviación de Cl⁻ a los 28 días, excepto en la combinación de CEM I SR.

	Método de ensayo	Unidad	Referencia	Marga yesífera	CEM I	CEM I SR	PC-8+GGBS	MCB100+GGBS	Sulfamag+GGBS
pH	Electrometría			8,6	11,3	11,5	10,5	10,3	10,9
Conductividad a 20°C	Electrometría	µS/cm		2240	2560	3200	2040	2060	2660
As disuelto	ICP/MS	mg/l	0,06	0,006	0,03	<0,0025	0,023	0,009	<0,0025
Cd disuelto	ICP/MS	mg/l	0,02	<0,001	<0,001	<0,0025	<0,001	0,001	<0,0025
Cr disuelto	ICP/MS	mg/l	0,1	<0,003	0,099	0,10851	0,005	0,009	<0,0025
Pb disuelto	ICP/MS	mg/l	0,15	<0,002	0,003	<0,0025	0,003	0,004	<0,0025
Ni disuelto	ICP/MS	mg/l	0,12	0,018	0,014	0,00421	0,011	0,007	<0,0025
Hg	ICP/MS	mg/l	0,002	<0,001	<0,001	<0,001	0,001	<0,001	<0,001
Ca	Absorción atómica	mg/l	-	665	533	557	516	504	550
Mg	Cromatografía iónica	mg/l	-	29	0,1	<0,2	0,31	0,42	<0,2
SO ₄	Cromatografía iónica	mg/l	1500	1626	1801	1450	1524	1583	1370
Cl ⁻	Cromatografía iónica	mg/l	450	13	<3,0	<20	<3,0	<3,0	<20
Total sólidos disueltos	Gravimetría	mg/l	-	2562	3035	2550	2421	2652	2550

Tabla 12. Resultados de lixiviación a 28 días

	Método de ensayo	Unidad	CEM I	CEM I SR	PC-8+GGBS	MCB100+GGBS	Sulfamag+GGBS
pH	Electrometría		11,3	11,4	10,9	11	11,1
Conductivity a 20°C	Electrometría	µS/cm	3370	3380	2620	2790	2750
As disuelto	ICP/MS	mg/l	<0,1	<0,1	<0,0025	<0,1	<0,0025
Cd disuelto	ICP/MS	mg/l	<0,1	<0,1	<0,0025	<0,1	<0,0025
Cr disuelto	ICP/MS	mg/l	<0,1	0,272	<0,0025	<0,1	<0,0025
Pb disuelto	ICP/MS	mg/l	<0,1	<0,1	<0,0025	<0,1	<0,0025
Ni disuelto	ICP/MS	mg/l	<0,1	<0,1	<0,0025	<0,1	<0,0025
Hg	ICP/MS	mg/l	<0,04	<0,4	<0,001	<0,04	<0,001
Ca	Absorción atómica	mg/l	553	571	536	561	550
Mg	Cromatografía iónica	mg/l	<0,2	<0,2	<0,2	<0,2	<0,2
SO ₄	Cromatografía iónica	mg/l	1550	1560	1370	1490	1410
Cl ⁻	Cromatografía iónica	mg/l	<20	<20	<20	<20	<20
Total sólidos disueltos	Gravimetría	mg/l	2840	2880	2410	2590	2380

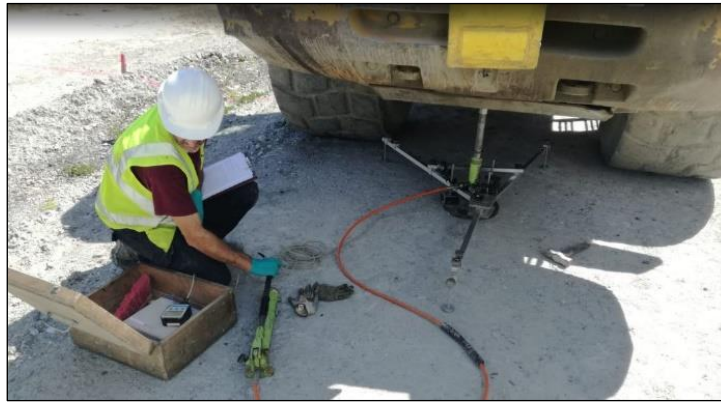
Tabla 13. Resultados de lixiviación a 90 días

De la investigación realizada en la zona de pruebas de campo, se desprenden como más relevantes las siguientes consideraciones:

- Después de 40 días desde la ejecución de la zona de pruebas de campo, las combinaciones de CEM I, CEM I SR, CL-90-S + GGBS y Sulfamag + GGBS mostraron en superficie signos evidentes de daños por hinchamiento, con valores de módulos de deformación vertical E_{v1} y E_{v2} (ensayo de carga con placa según UNE 103808) muy inferiores a los obtenidos en la zona de suelo sin estabilizar. Esto se atribuyó a la formación de minerales expansivos que provocaron la destrucción de los compuestos cementantes y de la propia estructura del suelo, con un importante descenso de la capacidad de carga de estas combinaciones. CEM I, CEM I SR y CL-90-S + GGBS también mostraron aumentos importantes en la relación de módulos E_{v2}/E_{v1} que evidenciaron la baja eficacia de la estabilización con aditivos ricos en calcio. Por otro lado, PC-8+GGBS y MCB100+GGBS mostraron módulos E_{v1} y E_{v2} a los 40 días muy superiores a los del suelo sin estabilizar, y una disminución de la relación de módulos E_{v2}/E_{v1} . Esto resalta la eficacia de los aditivos a base de magnesio para la estabilización del suelo yesífero. También se observó una diferencia notable en los módulos E_{v1} y E_{v2} de todas las combinaciones al comparar los valores obtenidos a 40 y 140 días. Esto se debió a las diferencias de humedad del suelo causadas por las precipitaciones acumuladas entre las dos fechas de ensayo (siendo de 284 mm/m² en una estación meteorológica situada a dos km de la zona de pruebas). A pesar de esto, las combinaciones de PC-8+GGBS y MCB100+GGBS alcanzaron relaciones de módulos E_{v2}/E_{v1} de 1,9 y 1,4 respectivamente, inferiores al valor de 2,2 requerido para los suelos estabilizados según la instrucción española de construcción de carreteras (Ministerio de Fomento, 2015).

Dosificación de aditivo (5%)	40 DÍAS			140 DÍAS		
	E_{v1} (MPa)	E_{v2} (MPa)	E_{v2}/E_{v1}	E_{v1} (MPa)	E_{v2} (MPa)	E_{v2}/E_{v1}
Marga yesífera	46	162	3,5	27	139	5,1
CEM I	8	55	6,9	28	82	2,9
CEM I SR	7	44	6,3	9	116	12,9
CL-90-S+GGBS	7	85	12,1	-	-	-
PC-8+GGBS	113	156	1,4	34	63	1,9
MCB100+GGBS	69	117	1,7	57	80	1,4
Sulfamag+GGBS	19	54	2,8	29	65	2,2

Tabla 14. Resultados de ensayos de carga con placa



Fotografía 7. Ejecución del ensayo de carga con placa



Fotografía 8. Aspecto de la zona de pruebas CEM-I-SR tras 40 días desde su estabilización



Fotografía 9. Zona CEM-I-SR con signos evidentes de hinchamiento

- Se evidencia así la importancia de la disponibilidad de agua y las circunstancias en las que la presencia de esta puede variar, para realizar valoraciones sobre el comportamiento de los cementantes en la estabilización de suelos con alto contenido en sulfatos. También es destacable la necesidad de extrapolar investigaciones científicas realizadas en laboratorio a una escala mayor y en condiciones ambientales diversas.

5.3.2.- ARTÍCULO 5: Estudio experimental de valorización de suelos con sulfatos para uso como material de construcción

Introducción

Este artículo recoge la investigación experimental llevada a cabo en laboratorio para la estabilización de un suelo con sulfatos, realizándose dicho proceso de estabilización en dos fases. Una primera fase donde se trató de consumir todo el sulfato presente en el suelo a través de su transformación controlada en etringita y una segunda fase donde el suelo se estabilizó mediante el uso de diferentes aditivos ricos en óxidos de calcio o magnesio, combinados con subproductos o residuos ricos en óxidos de aluminio o silicio reactivos.

Materiales empleados.

El suelo utilizado en esta investigación fue una muestra de lutitas margosas recogida en el municipio de Tudela (España). Este suelo presentaba un contenido en sulfatos solubles del 11%, conteniendo como principales fases minerales cuarzo, calcita, moscovita, dolomita y clorita. Este suelo se clasifica según el Sistema Internacional de Clasificación de Suelos (USCS) como ML y según la Instrucción de Carreteras de España (Ministerio de Fomento, 2002), como "suelo marginal".

Como aditivos estabilizantes se empleó una cal hidratada comercial CL-90-S como fuente de calcio para los tratamientos de estabilización, así como diferentes subproductos y residuos ricos en óxidos de magnesio, silicio y aluminio, adecuados para la estabilización del suelo: PC-8, cenizas volantes de cáscara de arroz (RHFA), cenizas de fondo (CBA) y filler de aluminio (AF). El PC-8 es el mismo polvo de horno rico en magnesio utilizados en los artículos precedentes. RHFA y CBA son residuos de la combustión en plantas de energía industrial de cáscara de arroz y carbón, respectivamente. AF se genera durante el proceso de valorización de las escorias salinas de fundiciones de aluminio.

Óxidos (%)	Cal	PC-8	RHFA	CBA	AF
CaO	-	8,5	-	38,5	1
MgO	-	72	-	11,4	6
Ca(OH) ₂	97,8	-	-	-	-
SiO ₂	-	3,5	99	36,6	8
Al ₂ O ₃	-	-	-	9,2	70

Tabla 15. Composición química de los aditivos empleados

Tipos de muestras analizadas y métodos

Para la investigación de laboratorio se tomó una tonelada del suelo, siendo triturada hasta un tamaño máximo de 2 mm y homogeneizada. Este suelo se caracterizó mediante ensayos de laboratorio, realizando ensayo de Proctor Normal (con un valor de densidad máxima de 1,79 g/cm³ y un contenido de humedad óptimo del 14,2%), límites de Atterberg (con un valor de límite Líquido de 24 y un índice de plasticidad de 3) e hinchamiento libre en edómetro (donde no se observó hinchamiento).

La primera fase de la estabilización del suelo fue la conversión del sulfato en etringita. Se establecieron tres dosis de cal + CBA para garantizar la disponibilidad de los óxidos necesarios para la formación de la etringita y el consumo total del sulfato del suelo, estas fueron: 3% de cal + 5% de CBA (COMB 1), 5% de cal + 5% de CBA (COMB 2) y 8% de cal+ 5% de CBA (COMB 3), considerando el % en peso. También se añadió a cada combinación un exceso de agua para la formación de la etringita, estimándose esta como el agua necesaria para alcanzar el contenido de humedad óptimo Proctor Normal más el agua necesaria estequiométricamente para la transformación del sulfato del suelo en etringita. Tras el mezclado de las distintas combinaciones (suelos, aditivo y agua), las muestras se colocaron en recipientes cerrados para evitar la desecación

y se mantuvieron a 40 °C hasta las edades de ensayo de 4, 8, 19, 27 y 52 días, realizándose a dichas edades XRD para cuantificar la etringita formada. Se consideró dicha temperatura para acelerar la formación de la etringita y evitar la pérdida de agua molecular en los minerales del suelo. Una vez establecida la dosis de aditivos más efectiva para la formación de la etringita, se preparó una nueva muestra de la combinación óptima con 300 kg de suelo de esta manera, suficiente para el resto del proceso experimental.

La segunda fase del tratamiento de estabilización fue mejorar la resistencia mecánica del suelo. Para lograr este objetivo, se mezcló el suelo modificado con cal CL-90-S o PC-8 (en un total de 7 combinaciones), como fuentes de cationes Ca²⁺ y Mg²⁺, así como con otros aditivos ricos en óxidos de aluminio y/o silicio. Una vez garantizada la homogeneidad de las muestras, se agregó el agua correspondiente al ensayo Proctor Normal de cada combinación, previamente determinado. Una vez lograda la homogeneidad de la humedad de las muestras, se fabricaron especímenes cilíndricos de acuerdo con el ensayo Proctor Normal. El curado de cada muestra se realizó en una bolsa de plástico cerrada en una cámara de humedad a 20 °C y una humedad relativa del 100% hasta las edades de 7, 14 y 28 días en las que se determinó su resistencia a compresión simple.

Combinación	Aditivos
1	SUELO MODIFICADO
2	SUELO MODIFICADO + 4% CAL + 5% RHFA
3	SUELO MODIFICADO + 4% CAL + 5% CBA
4	SUELO MODIFICADO + 4% CAL + 5% AF
5	SUELO MODIFICADO + 4% PC8 + 5% RHFA
6	SUELO MODIFICADO + 4% PC8 + 5% CBA
7	SUELO MODIFICADO + 4% PC8 + 5% AF

Tabla 16. Combinaciones seleccionadas para determinación de resistencia a compresión simple.

Análisis de resultados y conclusiones

Del primer paso de la estabilización se desprenden como más relevantes las siguientes consideraciones:

- Para las tres dosis consideradas, se formó etringita hasta la edad de 27 días, no incrementándose su contenido a partir de esta edad. La cantidad total de etringita producida por las tres combinaciones fue muy similar, con contenidos estimados por DRX entre un 4% y 5%. Basándonos en estos resultados, se eligió el tratamiento con un 5% de cal y un 5% de CBA (COMB 2) para la segunda parte del tratamiento de estabilización. A pesar de que las combinaciones 1 y 2 produjeron la misma cantidad de etringita, se eligió la combinación 2 para la modificación del suelo para evitar las incertidumbres en la realización de este tratamiento y asegurarse de que todo el sulfato del suelo se consumiera. Por otro lado, la

formación de solo un 1% más de etringita no se consideró suficiente para justificar el aumento de la dosis de cal hasta un 8%.

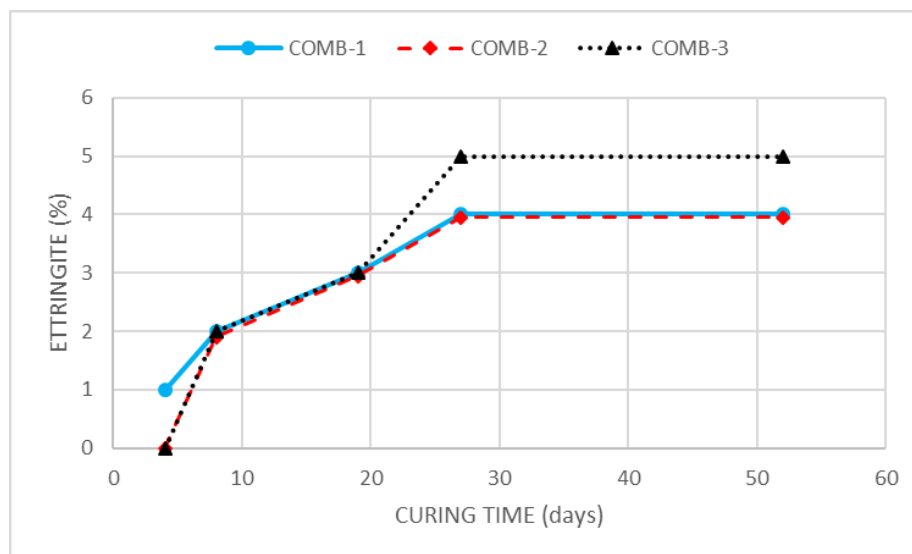


Figura 34. Evolución temporal de formación de etringita en las tres combinaciones

- Realizado al suelo el pretratamiento seleccionado, el valor de densidad máxima de Proctor Normal se redujo de 1,79 g/cm³ (suelo sin tratar) a 1,37 kg/cm³, aumentando el contenido óptimo de humedad del 14,2% al 30,5%. Esta reducción en la densidad del suelo se atribuyó a la formación de etringita y su menor densidad debido a su alto grado de hidratación. La nueva humedad óptima se determinó secando las muestras a 100 °C, lo que justifica el aumento en la humedad obtenida, ya que, además del agua libre, se eliminó también el agua de constitución mineral integrada en la etringita formada. El suelo modificado no presentó plasticidad y el hinchamiento libre en edómetro fue del 0,0%. La resistencia a la compresión del suelo modificado a los 7, 14 y 28 días alcanzó los 0,46, 0,49 y 0,61 MPa, respectivamente, mostrando un ligero aumento en comparación con el suelo natural.

Del segundo paso de la estabilización se desprenden como más relevantes las siguientes consideraciones:

- El uso de los aditivos de la segunda fase de estabilización incrementó el valor de densidad máxima Proctor Normal. Para las combinaciones 2 y 5, el valor de humedad óptima no se modificó respecto a la del suelo tratado. Esto indicó que, en estas combinaciones, las diferencias observadas dependen principalmente del RHFA. Con un comportamiento diferente, las combinaciones 3, 4, 6 y 7 alcanzaron resultados de densidad máxima muy cercanos entre sí y mostraron una reducción en el valor de humedad óptima. Esta reducción es más evidente para el PC-8 que para la cal y para la FA que para el CBA, demostrando la influencia de ambos constituyentes del aglutinante en el contenido óptimo de humedad de las combinaciones.

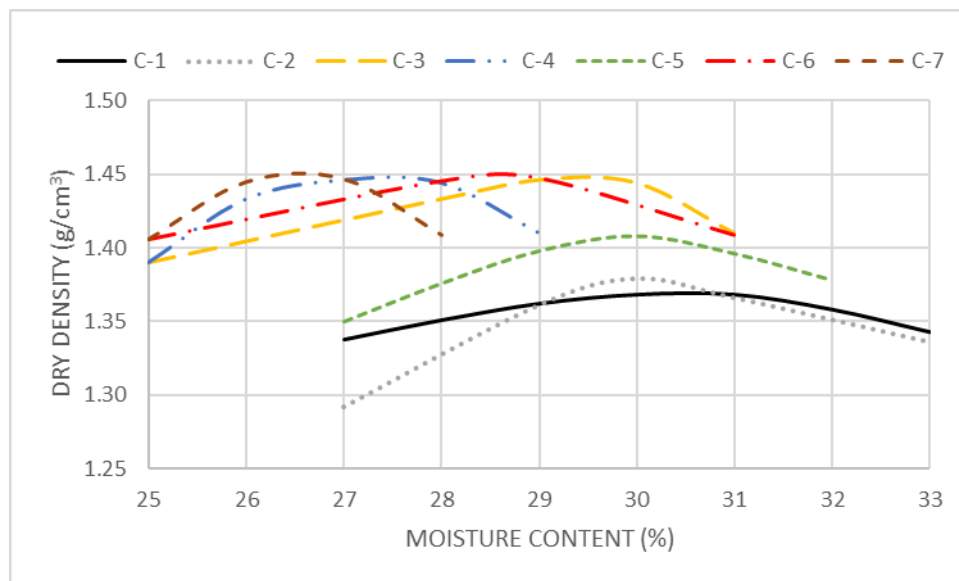


Figura 35. Curvas Proctor Normal de las distintas combinaciones del segundo paso de estabilización

- En cuanto al ensayo de resistencia a compresión simple, el suelo modificado alcanzó una resistencia de 0,45 MPa a los 7 días, 0,49 MPa a los 14 días y 0,61 MPa a los 28 días. Esto refleja un aumento en la resistencia a la compresión del suelo modificado en comparación con la del suelo natural. El pequeño aumento en la resistencia observado a lo largo del tiempo de curado probablemente se debe al efecto cementante de los iones de Ca^{2+} que no se consumen en la formación de etringita, los cuales generan reacciones puzolánicas en el suelo modificado.
- Las muestras modificadas tratadas con una mezcla de cal + RHFA (combinación 2) y cal + CBA (combinación 3) mostraron resistencias a la compresión simple de 0,87 y 0,55 MPa a los 7 días, 0,91 y 0,89 MPa a los 14 días, y 1,53 y 0,91 MPa a los 28 días, respectivamente. Estos aumentos en la resistencia se atribuyeron a la formación de geles cementantes en el suelo, debido a la disponibilidad de óxidos de calcio, silicio y aluminio. Algo similar ocurre con las combinaciones de mezcla de PC-8 + RHFA (combinación 5) y PC-8 + CBA (combinación 6), que alcanzaron resistencias a la compresión no confinada de 1,01 y 0,62 MPa a los 7 días, 1,69 y 0,74 MPa a los 14 días y 2,69 y 0,93 MPa a los 28 días, respectivamente. La combinación de PC-8 + RHFA logró mejores resultados de UCS que la mezcla de cal + RHFA, demostrando un mejor comportamiento del MgO del PC8 en comparación con la cal como activador de fuentes de Si y Al para la formación de geles hidráulicos cementantes, de acuerdo con Seco et al. (2017).

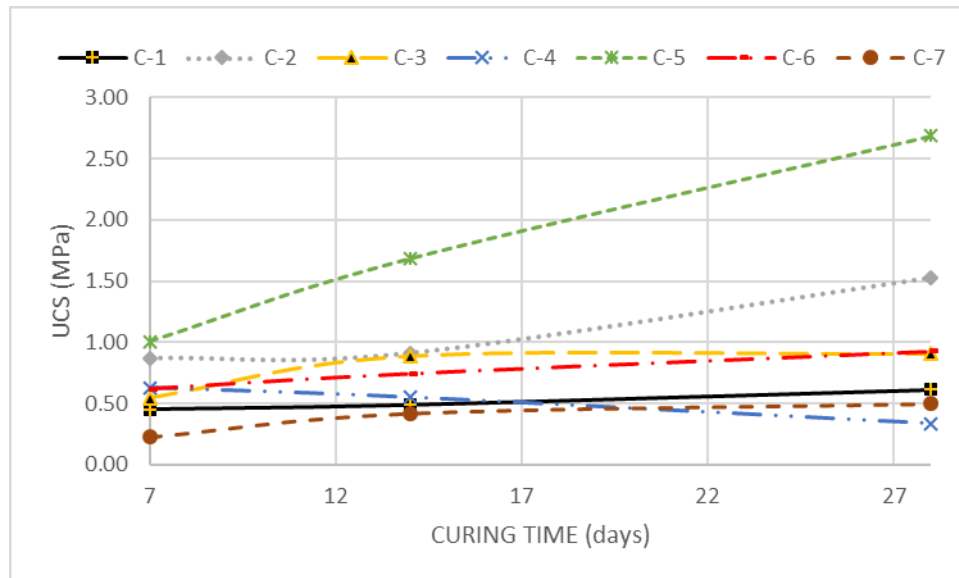


Figura 36. Resultados del ensayo de compresión simple

- Las combinaciones con AF mostraron resultados anómalos en comparación con las obtenidas con las otras fuentes de Si y Al. En la combinación 4 (mezcla de cal + AF), los valores de resistencia a la compresión simple disminuyeron de 0,63 MPa a los 7 días a 0,55 MPa a los 14 días y 0,33 MPa a los 28 días. Dado que el óxido de aluminio es uno de los minerales involucrados en la formación de etringita, estos bajos valores de resistencia se atribuyeron a la formación de más etringita, lo que derivó a un hinchamiento en la muestra con alteración de su estructura. Para la combinación 7 (PC-8 + mezcla de AF), los valores de resistencia a la compresión alcanzaron 0,23 MPa a los 7 días, 0,42 MPa a los 14 días y 0,50 MPa a los 28 días. El aumento en los valores de resistencia de esta combinación demuestra, una vez más, la eficacia del MgO en la formación de geles cementantes, sin comportamiento expansivo, incluso en entornos ricos en aluminio.

6.- CONCLUSIONES GENERALES

La tesis aquí expuesta, pretende aportar algo más de conocimiento para la generación de cementantes aplicables en el sector de la construcción y la ingeniería civil, que puedan dar solución a un problema constructivo mundial como es la estabilización de suelos con alto contenido en sulfatos. Si bien la investigación científica permite ahondar en el conocimiento, no es menos cierto que durante su desarrollo se van generando nuevos interrogantes, exponiéndose a continuación las conclusiones y cuestiones encontradas a lo largo de esta búsqueda de conocimiento.

Campaña experimental FASE 1

Los cementantes hidráulicos a base de MgO experimentados han demostrado su potencial para su uso en construcción. Si bien presentan tiempos de curado más elevados que los de los cementos comunes (debido a una menor capacidad de hidratación y una menor reactividad), han demostrado que pueden alcanzar y superar sus resistencias. Por otro lado, estas cualidades presentan un amplio rango de aplicaciones relacionadas con obras de hormigón de gran volumen donde el calor de hidratación del cemento es un problema (como grandes presas de hormigón en masa).

Se han evidenciado las buenas propiedades mecánicas de los sistemas cementantes M-S-H en comparación con los C-S-H a edades largas de curado. También se ha constatado la potencialidad del polvo de horno de calcinación de magnesita identificado como PC-8. Este subproducto presentó mejores prestaciones para la formulación de cementantes que otros productos comerciales de óxido de magnesio. Se amplía así el campo de investigación sobre las mejores condiciones de generación de MgO reactivo dependiendo de tiempos y temperaturas de calcinación.

Se ha demostrado que también el MgO procedente de residuos de refractario agotado SRW puede tener ciertas aplicaciones en la formulación de materiales de construcción sostenibles (gránulos) así como formar parte de los cementantes con sistemas M-S-H. Los SRW empleados en esta tesis demostraron una reactividad residual que podría beneficiar la fabricación de áridos reciclados con propiedades mejoradas. También mostraron una importante capacidad de carbonatación (con CO₂ ambiental), con cambios importantes en las propiedades físicas de los gránulos fabricados.

Campaña experimental FASE 2

En esta campaña experimental se estableció una baja reactividad de residuos de material refractario agotado y su limitada, aunque no nula, capacidad para la estabilización de un suelo arcilloso. En fase experimental se evidenció que la capacidad de estabilización no solo depende de la capacidad y características del cementante, sino también de la naturaleza y características de los suelos. Presentando los suelos variabilidades en sus características físicas y geotécnicas tan amplias, el grado de afección de un cementante puede también ser muy variable.

Campaña experimental FASE 3

En esta fase se ha demostrado la capacidad de cementantes hidráulicos basados en el magnesio para la estabilización de suelos con alto contenido en sulfatos, evitando los efectos adversos que presentan el uso de la cal y el cemento Portland. Se ha verificado que cementantes formulados con GGBS (como fuente de silicio y aluminio) + MgO procedente de polvo de horno de calcinación de magnesita, son una alternativa eficaz para la estabilización de estos suelos.

Se evidenció que el empleo de cemento sulforresistente en la estabilización de un suelo con sulfatos, no evita los efectos adversos de la formación de etringita. La expansividad derivada de la formación de esta fase mineral se manifestó tanto en laboratorio como en la prueba de campo, donde presentó un comportamiento similar al cemento no sulforresistente. Sin poner en duda su buen comportamiento en la fabricación de hormigones, la efectividad de los cementos sulforresistentes no solo depende de su composición química, sino que además requiere de un entorno de baja permeabilidad y de condiciones de humedad estables, algo que no es fácil asegurar cuando se emplea en la estabilización de suelos.

También se ha evidenciado las limitaciones de la experimentación en laboratorio, dentro del campo de la estabilización de suelos. La zona de pruebas de campo demostró los problemas derivados de la formación de etringita al emplear cal y cementos para la estabilización, mientras que esta evidencia no se observó de forma tan clara en la fase experimental previa de laboratorio. Se pone así de manifiesto, la importante influencia de la escala en la realización de ensayos y en la representatividad de los resultados, así como de las condiciones ambientales en las que se llevan a cabo. Esto nos lleva a la necesidad de pruebas piloto con distintos tipos de suelos y distintas condiciones ambientales, algo que necesariamente requiere de la implicación de estamentos y administraciones públicas responsables del desarrollo y mantenimiento de vías de comunicación terrestres.

7.- FUTURAS LINEAS DE TRABAJO

De las conclusiones generales expuestas, quedan abiertas varias líneas de trabajo, destacando la importancia de la escala (temporal, espacial y ambiental) en el diseño de ensayos para la estabilización de suelos. En futuras investigaciones deberá analizarse también la influencia de las variaciones y condiciones ambientales: humedad, temperatura, insolación, procesos de heladicidad, estacionalidad, etc.

También se considera que debe ampliarse la experimentación con suelos de distinta naturaleza, buscando posibles contraindicaciones que los cementantes basados en el magnesio pudieran producir en la estabilización, como pudiera ser la estabilidad o reversibilidad de los compuestos cementantes generados ante la presencia de algún agente físico o químico.

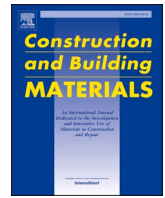
En cuanto a la formulación de cementantes basados en la combinación de GGBS + MgO queda abierta la búsqueda de fuentes alternativas al GGBS como fuente de Si y Al. A pesar de la conveniencia del GGBS como aditivo estabilizador y del hecho ser un subproducto de la fabricación del hierro, el GGBS es un producto escaso y costoso, que en la actualidad casi en su totalidad se consume en la industria del cemento.

El equipo de investigación en el que se ha desarrollado la presente tesis, mantiene abiertos muy prometedores proyectos para el desarrollo de cementos de bajo impacto ambiental, como son los cementos de oxisulfato de magnesio, formulados también a partir de residuos y subproductos del proceso de obtención de material refractario a partir de magnesita. Ya se han formulado morteros de elevadas resistencias mecánicas a partir de este cementante, contradiciendo la baja resistencia comúnmente asociada a este tipo de cemento (Guo et al., 2017). También se están estudiando y desarrollando cementos sobresulfatados formulados con sustitución de clinker por minerales arcillosos. Queda abierta la posibilidad de empleo de estos cementantes también en la estabilización de suelos.

BLOQUE B

8.- PUBLICACIONES CIENTÍFICAS

ARTÍCULO 1



Assessment of the ability of MGO based binary binders for the substitution of Portland cement for mortars manufacturing

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ABSTRACT

This article evaluates the ability of a magnesia kiln dust (PC-8) and a commercial calcined MgO (MCB100), combined with ground granulated blastfurnace slag (GGBS), as constituents of binary M-S-H binders. Mortars and pastes were manufactured and their properties were compared to those of Portland Cement (PC). MgO-based mortars showed an increase in setting time and higher fresh consistency. At earlier ages MgO mortars showed lower mechanical properties. At 90 days both MgO-based mortars overcame the PC flexural strength and PC-8 + GGBS also overcame its compressive strength. X-Ray Diffraction and Thermogravimetry tests demonstrated the presence of M-S-H in the pastes.

1. Introduction

MgO-based hydraulic binders are receiving increasing interest because of their potential as alternative to Portland Cement (PC). Reactive MgO in MgO-SiO₂-H₂O systems form poorly ordered nanosized phyllosilicates with cementitious properties known as magnesium silicate hydrates (M-S-H) [1-3]. Nowadays most of MgO is obtained by calcination of natural magnesite rocks (MgCO₃) that, by firing, decarbonize as shown in Eq. (1), releasing about 1.1–1.4 kg of CO₂ for the production of 1 kg of MgO [4-6].



The most important parameter of the magnesite rocks calcination is the calcining temperature as it determines the properties of the MgO manufactured. Below 1,000 °C MgO crystals have lower size, high porosity and high specific surface area (SSA). As a result, MgO shows a high level of reactivity. Increasing the calcination temperature at > 1,000 °C, MgO crystals' size increases and SSA and reactivity reduces [4,7-9]. Magnesite is a scarce and expensive raw material that is mainly consumed for the manufacturing of refractory materials for the industry [10]. Commercial magnesite calcination is carried out in rotary kilns with crosscurrent air as shown in Fig. 1.

Magnesite rocks enter in the combustion chamber and advance as the

kiln rotates. As magnesite advances it is heated and thereby decarbonized by the combustion gases and the direct flame of the fuel burning. After burning calcined magnesite is air cooled before leaving the kiln. During the calcination, the countercurrent flow pulls dust magnesite particles along the combustion chamber that are collected in cyclones before the venting of gases to the atmosphere. This magnesia kiln dust (MKD) contains a mix of unburned magnesite, calcined MgO and eventually sintered MgO, depending on the part of the combustion chamber where they were pulled from and the higher temperature they were exposed to. The amount of MKD production supposes about 30% of the calcined magnesite manufactured and it is usually marketed as a low grade MgO byproduct. Published works have demonstrated the MKD ability as a binder constituent for clay, expansive and sulfate soils stabilization [11-13] and for the unfired clay bricks manufacturing [14,15]. Nonetheless, nowadays the total consumption of MKD is lower than its production, being an increasing economic and environmental concern for the MgO industry, due to the world growing needs of refractory materials [16]. Thus, new applications for this low grade reactive MgO are required. The aim of this study has been to evaluate the ability of a MKD and a commercial reactive MgO, combined with ground granulated blastfurnace slag (GGBS), as constituents of binary M-S-H binder systems for the production of ordinary masonry mortars. For this, an experimental laboratory investigation of MKD-GGBS and MgO +

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GGBS mortars and pastes was carried out. PC was considered as reference. Fresh consistency, setting time, density, flexural strength and compressive strength tests were conducted to characterize the magnesium-based mortars fresh and cured properties as construction materials. pH, X Ray Diffraction (XRD) and thermogravimetric analysis were carried out to state the M-S-H gels formation.

2. Materials and methods

2.1. Materials

Two MgO sources were used in the laboratory investigation: A high reactive commercial MgO obtained from magnesite rocks calcined at 1,100 °C, marketed as MCB100. The second MgO material was a MKD recovered from the combustion gases of two kilns, working at 1,100 °C and 1,800 °C respectively. This co-product is marketed under the name PC-8. Both MgO samples were supplied by *Magnesitas Navarras S.A.* company that produce them in its factory located in Zubiri (Spain). [Table 1](#) shows the chemical composition, parameters representative of the reactivity and [Fig. 2](#) shows the granulometry of the constituents of the binders considered for the laboratory investigation.

GGBS is a by-product obtained during the manufacturing of pig iron. It is formed by rapid cooling of molten iron slag to maintain an amorphous structure and it is grinded in order to increase its reactivity. The sample available for this investigation was provided by Heidelberg Cement Group (UK). As shown in [Table 1](#), it has a big cementitious potential because of its richness in reactive calcium, silicon and aluminum oxides. PC used in this study was manufactured in accordance with the European Standard EN 197-1 and is marketed in Spain under the trade name CEM II/B-L 32.5 N. As aggregate for the mortars manufacturing a commercial calcareous 0–4 mm sand from limestone crushing was used.

2.2. Samples preparation

Pastes and mortars were manufactured for the laboratory investigation. Fresh and cured binder characterization tests were carried out on mortar samples meanwhile XRD and thermogravimetric tests were conducted on pastes. For the paste and mortar samples manufacturing, MgO product to GGBS binder proportion chosen was 20 wt% to 80 wt%. For the PC pastes and mortar samples manufacturing, the ratio water to cement was fixed in 1 to 2.5 ($w/c = 0.4$). For the MgO product samples, the ratio water to binder was fixed in 1 to 1.5 ($w/b = 0.6$) because of the MgO product mortars workability needs, in accordance with [\[17-21\]](#). MgO products and GGBS were mixed in a laboratory mortar mixer for 5 min to guarantee the binder homogeneity. For the pastes manufacturing, water was added to the mix of MgO product and GGBS or to PC and mixed for 10 min to guarantee the mix homogeneity and the correct moisture distribution. Paste samples were poured, vibrated and maintained in closed containers till the testing ages of 28 and 90 days. For the

Table 1

Chemical composition, fineness and reactivity of the MgO binder constituents and PC.

OXIDES (%)	PC-8	MCB 100	GGBS	PC
MgO	59.67	82.26	9.05	1.21
CaO	9.10	3.79	43.94	70.82
SO ₃	6.27	0.21	2.00	4.15
SiO ₂	2.80	3.41	32.18	14.12
Fe ₂ O ₃	2.34	2.90	0.33	4.10
Al ₂ O ₃	0.57	0.82	10.40	3.36
Loss of ignition at 1,050 °C	19.25	6.61	0.46	4.97
Reactivity in citric acid (min)	29	2	>600	>600
pH in water	10.66	10.88	9.82	11.88
Free lime (%)	0.81	1.04	0.28	3.67

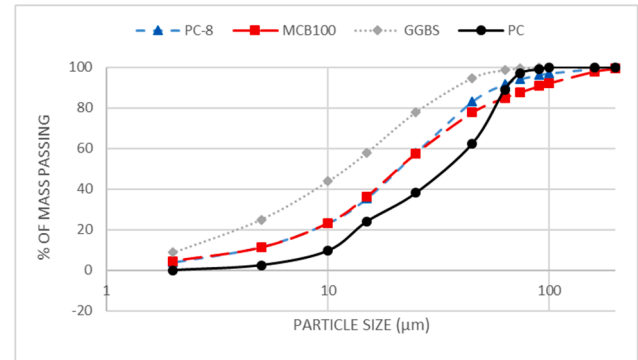


Fig. 2. Granulometric curves of the binder constituents.

mortars manufacturing, MgO products and GGBS were mixed in the same manner described for pastes. Sand was added to the binary binders or to PC and mixed for 5 min. Then water was added and mortars were mixed for 10 min. Fresh mortars were cast into 4x4x16 cm molds and compressed using a vibrating table for 30 s. After compaction, sample surfaces were manually smoothed and maintained in laboratory conditions for 24 h before unmolding. Unmolded mortar samples were cured in water immersion till the testing ages of 7, 14, 21, 28 and 90 days.

2.3. Fresh and cured properties testing methods

The fresh consistency of the mortars were evaluated using the flow table test, in accordance with the standard EN 1015-3. Mortars setting time was determined by means of the Vicat needle method, in accordance with the standard EN 480-2. Samples density was stated as the ratio between the dry mass of each specimen and its corresponding volume, measured by a digital caliper, in accordance with the EN 1015-10. The mechanical properties of the mortars were studied by means of the flexural (FS) and compressive strength (CS) at different curing ages.

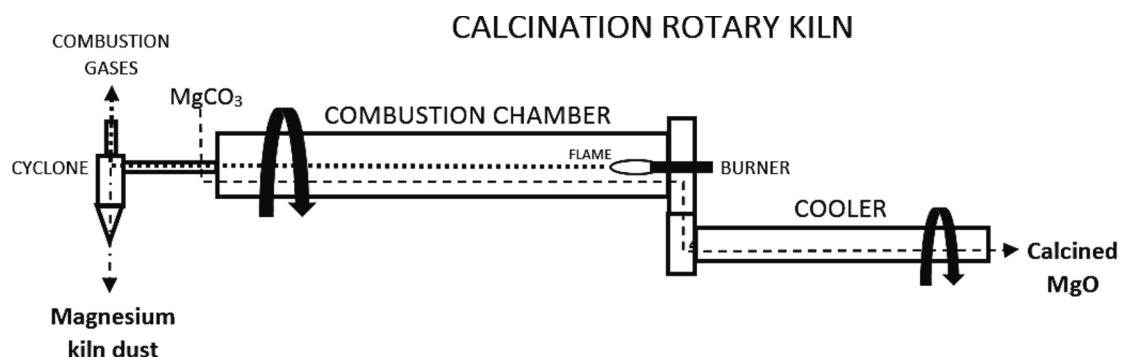


Fig. 1. MgO manufacturing process.

FS and CS tests were carried out in accordance with the standard EN 1015–11.

2.4. Chemical testing methods

At the considered testing ages, samples of each paste combinations were conditioned as follows to completely stop the cementation reactions: 50 g of each paste combination were ground and added to 250 g of isopropanol in a beaker. The mix was shaken with a glass stirrer for 1 min and the result was filtered adding an additional quantity of isopropanol to clean the beaker. Once filtered, the sample was collected and dried for 10 min in an extractor hood and after that the sample was maintained for 24 h at 40 °C in a stove. Once the sample was dried it was maintained in a closed plastic container with silica gel and a CO₂ sorbent till testing.

Specimen pH values were determined following the procedure published in [8]. 10 g of paste specimen samples were dispersed in 100 ml of distilled water. After an hour of mixing, solids were filtered and pH was measured by using a laboratory pH meter with an accuracy of ± 0.01. Crystalline phases and the hydration products present in the paste samples were investigated by XRD testing. This test was performed using a powder diffractometer D8-Advance, Bruker Corp. A Cu-K α X-ray tube with an input voltage of 40 kV and a current of 40 mA was employed. The samples were scanned for 2 theta value ranging from 4° to 70°, with a step length of 0.05°, scanning rate of 3°/min.

Consumption of MgO, hydration products and M-S-H gels formation were monitored at 28 and 90 days by thermogravimetric analyses (TGA/DTG) in a METTLER-TOLEDO TGA/DSC 3 + system. Tests were conducted with 10 mg of sample under an air flux of 100 ml/min and a heating rate of 10 °C/min from room temperature to 900 °C, with a N₂:O₂ (4:1) oxidizing atmosphere.

3. Results and discussion

3.1. Mortar fresh properties

Table 2 shows the mortar fresh properties.

The fresh consistencies of the mortars observed were 177 mm for the PC combination, 160 mm for the PC-8 + GGBS and 144 mm for the MCB100 + GGBS one. As all the samples were manufactured maintaining constant the aggregates to binder and water to binder ratios, the differences in consistency would be attributed to the binder constituents fineness [22–24]. As expected based on its coarser granulometry, PC mortar showed the lower consistency. Nevertheless the consistent differences observed between the PC-8 + GGBS and the MCB100 + GGBS mortars cannot be attributed only to the small granulometric differences between these two MgO products and would be due to differences of water affinity between PC-8 and MCB100.

The setting time of the considered mortars are provided in Table 2. The initial and final shorter setting times correspond to the PC sample, with 200 and 317 min respectively. PC-8 + GGBS and MCB100 + GGBS mortars showed an increase in initial and final setting times because of their lower pH and rate of pozzolanic reactions compared to PC [22,25].

Table 2
Fresh properties, densities and pH values of the mortars.

Test	Binder		
	PC-8 + GGBS	MCB100 + GGBS	CEM II 32.5
Flow table consistency (mm)	160	144	177
Setting time (minutes)			
Initial	458	478	200
Final	1261	1450	317
Dry density (g/cm ³)	1.88	1.88	1.96
pH			
28 days	11.43	11.47	12.00
90 days	11.49	11.70	12.09

PC-8 + GGBS reached shorter setting times than MCB100 + GGBS, showing its higher hydration ability.

3.2. Mortar cured properties

PC combination reached the highest mortar density, 1.96 g/cm³, demonstrating the ability of the C-S-H gels to form a denser structure compared to the M-S-H ones [10]. PC-8 + GGBS and MCB100 + GGBS combinations showed no density differences, achieving both mortars 1.88 g/cm³. The observed lower density of both MgO + GGBS mortars agrees with those obtained by Dave et al. [22] and highlights the direct effect of the binder fineness and the mortar density.

Fig. 3 shows the mortars flexural and compressive strength development up to 90 days.

PC samples showed quick flexural strength development due to its rapid hydration and high reactivity. At 7 days PC mortars reached 4.51 MPa which slowly increased till 5.25 MPa at 90 days. MCB100 + GGBS and PC-8 + GGBS mortars showed a direct flexural strength increase along the curing time. At the age of 7 days MCB100 + GGBS and PC-8 + GGBS mortars reached 1.02 MPa and 2.59 MPa of flexural strength respectively. At the age of 21 days PC-8 + GGBS samples showed a flexural strength of 4.99 MPa, very close to the 5.23 MPa obtained by PC. At the age of 90 days, MCB100 + GGBS and PC-8 + GGBS mortars overcame the PC result, achieving 6.49 MPa and 7.14 MPa, respectively. The lower flexural strength of the MgO-based mortars at the earlier curing ages is probably due to the slower hydration ability and reactivity of these binders, as stated by the setting times test and in accordance with the results obtained by Jin and Altabaa [19] and Bernard et al. [26]. Considering the calcining temperatures, reactivity parameters and fineness of PC-8 and MCB100, the higher flexural strength reached by the PC-8 + GGBS samples compared to these of MCB100 + GGBS is an

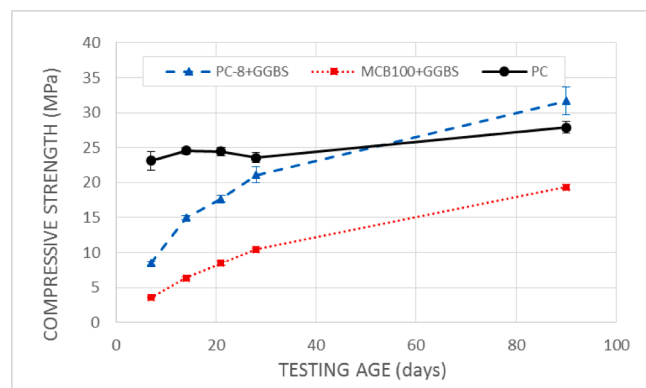
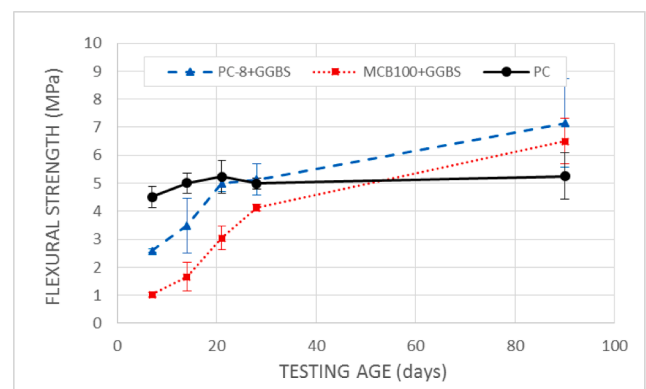


Fig. 3. Mechanical strength of the mortars. a) Flexural strength and b) Compressive strength.

unexpected result. It could be related to the content of CaO of the PC-8 that would hydrate to form C-S-H gels contributing to increase the flexural strength of the PC-8 + GGBS samples [27].

Compressive strengths of mortars are presented in Fig. 3-b. PC samples reached compressive strength of 23.11 MPa at the age of 7 days which increased slightly till 27.90 MPa at 90 days. This compressive strength development agrees with the flexural strength and highlights the quick hydration of the PC compared to the MgO-GGBS binary binders. MCB100 + GGBS and PC-8 + GGBS combinations showed a compressive strength development close to those observed in the flexural strength due to the pozzolanic gels formation [22,28,29]. As well as in the case of the flexural strength, PC-8 + GGBS samples showed higher compressive strength than MCB100 + GGBS at all the curing ages. At 7 days, MCB100 + GGBS mortar showed 3.57 MPa compressive strength, whereas PC-8 + GGBS reached 8.47 MPa. These values increased along the curing time till reaching 19.36 MPa for the MCB100 and 31.68 MPa for the PC-8 at 90 days. Only PC-8 overcame the PC compressive strength between 28 and 90 days.

Flexural and compressive strength test results demonstrated the convenience of the MgO + GGBS binary binders for the manufacturing of ordinary masonry mortars with the required mechanical properties. The higher ability of PC-8, a MKD, was also demonstrated, compared to MCB100, a commercial reactive MgO product, to form cementitious hydraulic gels, that achieved higher mechanical strength than PC.

3.3. Mortar chemical properties

pH values of the considered paste combinations at 28 days and 90 days are shown in Table 2. The pH of the pastes is related to the hydration of MgO and CaO that transform into $Mg(OH)_2$ and $Ca(OH)_2$ respectively, releasing OH^- to the paste dissolution. As expected PC, due to its high content of available CaO, reached pH values of 12.0 at 28 days and 12.08 at 90 days respectively, in accordance with Gu et al. [10] and Shen et al. [6], among others. PC-8 + GGBS paste showed pH values of 11.43 at 28 days and 11.47 at 90 days, while MCB100 + GGBS achieved 11.47 and 11.70 at the same curing ages. These relatively high pH values for MgO-based binders are probably due to the presence of CaO as well in both MgO products as in the GGBS [3,7,8,19]. All the binders showed very close results at both curing ages, probably due to the equilibrium of the precipitation-dissolution of M-S-H and C-S-H gels and $Mg(OH)_2$ and $Ca(OH)_2$ respectively [30].

Fig. 4 shows the XRD diffractograms of the PC, PC-8 + GGBS and MCB100 + GGBS pastes at 28 and 90 days.

MgO, $Mg(OH)_2$, $MgCO_3$ and $CaCO_3$ were identified in the diffractograms of the pastes of PC-8 + GGBS and MCB100 + GGBS based on Jin and al-tabbaa [7], Sonat et al. [8], 2017 and Tran and Scott [31]. MgO in the pastes is related to their periclase content, due to the calcination of the magnesite rock. Brucite appears as well as in the PC-8 + GGBS as in the MCB100 + GGBS pastes. Its presence demonstrated the existence of reactive MgO in the PC-8 and MCB100 and its ability to hydrate. The intensity of the brucite peaks was higher in the PC-8 + GGBS paste than in the MCB100 + GGBS one, showing a better hydration ability of this combination. For both MgO products, the intensity of the brucite peaks increased since 28 days to 90 days, due to the MgO hydration along the time. The presence of $MgCO_3$ and $CaCO_3$ in the pastes was attributed to non-calcined magnesite and calcite rocks. As expected based on their different degree of calcination, PC-8 containing sample showed a higher content of carbonates than MCB100 ones. M-S-H gels have a low crystallinity structure and they were identified as well as in the PC-8 + GGBS as in the MCB100 + GGBS pastes, as the broad peaks in the 17–28°, 32–39° and 58–62° range 2 θ angles [8,32–34].

Fig. 5 shows the TG and first derivative of TG (DTG) results of the binder pastes. Since all samples were thoroughly dried before testing, the loss of mass observed corresponds to the decomposition of hydrate phases [3,8,35]. The first decomposition step generates peaks in the DTG curves centered at about 90–105 °C. These peaks involve the loss of

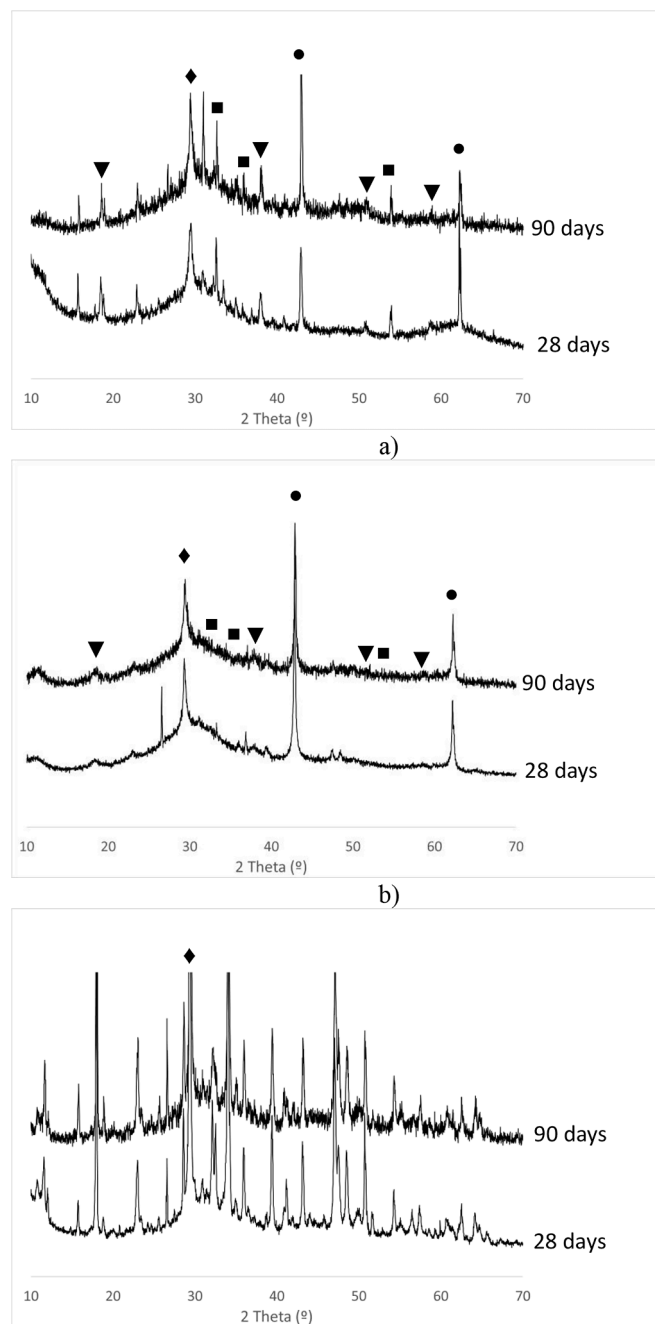


Fig. 4. XRD diffractograms of all paste samples at 28 and 90 days. a) PC-8 + GGBS, b) MCB100 + GGBS and c) PC. (●: MgO, ▼: $Mg(OH)_2$, ■: $MgCO_3$, ◆: $CaCO_3$).

poorly bound water absorbed in the surface and the interlayer of hydration product structures. Cement paste showed the highest loss of mass in this step, demonstrating a higher capacity of C-S-H gels compared to M-S-H ones for the physically bounding of water. PC-8 + GGBS achieved higher loss of mass than MCB100 + GGBS which could be related to the capacity of both binders to produce M-S-H gels, in accordance with the mechanical strength results. PC and MCB100 + GGBS showed a higher loss of mass at 28 days than at 90 days in accordance with the results obtained by Monteagudo et al. [36] but in contradiction with those of Jin and Al-Tabbaa [19]. On the other hand, PC-8 + GGBS reached very close results for both curing ages. This could be due to the different hydration processes and resulting products obtained by each binder because of their different reactivity. The second

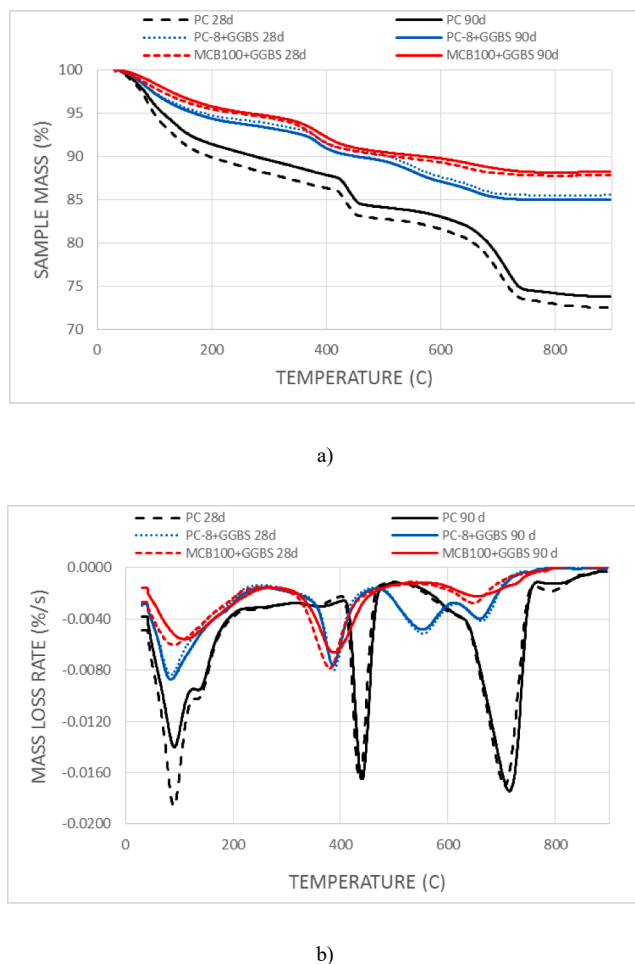


Fig. 5. Thermogravimetric analysis curves for the PC, PC-8 + GGBS and MCB100 + GGBS pastes at 28 and 90 days. a) TG and b) DTG.

decomposition step corresponds to the dehydroxylation of brucite and portlandite [35,37,38]. Thus, brucite decomposition is shown as a peak in the PC-8 + GGBS and MCB100 + GGBS DTG curves at about 390 °C. MCB100 + GGBS showed an expected reduction of this peak because of the brucite consumption from 28 days to 90 days [19]. This reduction was not visible in the PC-8 + GGBS DTG curve that points up the probable consumption of brucite before 28 days in this binder. At 440 °C PC curves show the portlandite dehydroxylation peak [38,39]. In PC-8 + GGBS DTG curves, a peak centered at about 560 °C is observed, corresponding to the M-S-H dehydroxylation or more probably to the magnesite decarbonation [2,7,8,26,40]. Above 650 °C till 750 °C calcite decarbonation occurs [37-39]. PC DTG curve shows a deep decarbonation peak corresponding to the PC limestone content. MCB100 + GGBS and PC-8 + GGBS pastes show in the DTG curves two peaks centered at 655 °C and 665 °C respectively, corresponding to the calcite decomposition [36,40]. The higher loss of ignition at 1,050 °C of the PC-8 compared to MCB100 points out its higher CaCO_3 content and would agree with these peaks intensity. Other authors attribute the losses of mass at these temperatures to the dehydroxylation of magnesium or silanol hydroxyl groups [3,8,33,41,42]. The mechanical strength results of the PC-8 + GGBS samples demonstrated the higher ability of this combination to produce M-S-H gels than MCB100 + GGBS one. This also could justify the peaks shown in the DTG curves at 655 °C and 665 °C. So both origins for these peaks are feasible as well as a possible overlapping of dehydroxylation and decarbonation effects [19].

4. Conclusions

In this paper binary binders have been prepared from a commercial and by-product MgO sources, combined with GGBS. The ability of both MgO products for the M-S-H systems formation was evaluated by means of the characterization of fresh mortar properties, mortars mechanical strength and pastes chemical properties. Both MgO binders required higher w/b ratio for workability. PC-8-based binder reached higher consistency than cement but lower than MCB100-based binder. Both MgO-based binders reached identical densities, and slightly lower than PC one, demonstrating the influence of these product fineness and the w/b ratio in the mortar densities. MgO-based binders greatly increase the initial and final setting times compared to PC, related to a lower ability for their hydration and lower reactivity. MgO-based binders showed initial lower mechanical strength that increased along the curing time. Both MgO based mortars overcame PC flexural strength before 90 days, having reached the PC-8 combination the highest flexural strength result. PC-8 containing binder also achieved the highest compressive strength. This demonstrate the good mechanical properties of M-S-H systems compared to the C-S-H at long curing ages ones, and the convenience of PC-8 to produce binary binders with GGBS, compared to MCB100. XRD tests demonstrated the ability of the MgO products to hydrate and to form M-S-H gels. TG/DTG test showed differences in the dehydroxylation, dehydroxylation and decarbonation processes between the M-S-H and the C-S-H systems of the binders considered. The differences observed between the PC-8 + GGBS and MCB100 + GGBS combinations were attributed to the differences of mineralogy and reactivity of both MgO sources. It should be noted that the results and conclusions obtained are applicable to the specific materials used in this investigation and that other MgO products may produce different results. As final conclusion, the higher potential of the MKD as binder component for the mortars manufacturing can be stated, compared to the commercial MgO source. Its longer setting times and higher physical strength are properties with a very wide application range related with large concrete works. Further investigations related with massive concrete structures would be developed, where hydration heat could be more easily dissipated for possible enhancement of the concrete retraction capacity.

Data availability.

The raw data required to reproduce these findings are available from the authors.

CRediT authorship contribution statement

A. Seco: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **J.M. del Castillo:** Methodology, Formal analysis, Investigation, Writing – review & editing. **S. Espuelas:** Investigation, Writing – review & editing. **S. Marcelino:** Resources, Investigation, Visualization, Project administration. **A.M. Echeverría:** Data curation, Investigation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ARTÍCULO 2



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Recycled granulates manufacturing from spent refractory wastes and magnesium based binder

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ABSTRACT

This paper analyzes the ability of two Spent Refractory Wastes (SRW) for the manufacturing of recycled granulates for construction applications. A binary magnesium oxide and ground granulated blast furnace slag hydraulic binder was considered as an agglomerating agent for the granulates manufacturing. Influence of curing atmosphere was carried out: in air, 20 % CO₂ and 100 % CO₂ atmosphere up to 28 days. Granulometry, thermal analysis, particle density, bulk density, water absorption and mechanical strength tests were performed to characterize the granulates. SRW showed their ability for the granulates manufacturing. Results demonstrated the existence of a residual reactivity of the wastes considered. A direct relationship between the CO₂ content of the curing atmosphere and the granulates hydration degree was observed. Carbonation process increased from 7 days to 28 days and direct relationships were observed between the CO₂ content and the carbonation degree as well as between the binder dosage and the carbonation degree. CO₂ curing reduced the water absorption and increased the compressive strength of the granulates.

1. Introduction

Magnesia refractories are indispensable lining materials of high temperature vessels for steel manufacturing. They are ceramic materials mainly composed of periclase, obtained from calcined magnesite, that coat the inside of vessels to withstand the high temperatures reached by the molten metal during the production process. This industry consumes between 8 kg and 15 kg of refractory materials per ton of manufactured steel [1,2]. The EU is the second largest producer of steel in the world after China with an output of over 177 million tons per year [3]. This represents an estimated production of spent refractories between 1.42 and 2.66 million tons a year, in the EU alone. For the last two decades, the interest in the valorization of spent refractories has increased due to environmental regulations, increasing costs for landfilling and raw materials preservation. Magnesia spent refractories are composed of two main fractions, with different characteristics, depending on their exposure to the molten metal. The outer refractory part, that has been in contact with the molten metal, shows slag and metal penetration through the periclase recrystallization cracks. This fraction contains a

loss of magnesia and higher silicon concentration because of its migration from the refractory inside to the outside magnesia refractory part. On the other hand, the inner part, which has not been in contact with the molten metal, shows a chemical composition that does not differ much from the refractory nominal composition. The sintering differences generated by the lower temperatures it is submitted to makes the inner part more friable than the outer one [1]. Previous to their valorization, refractory debris require a selection and cleaning process. It is usually carried out by means of a crushing, screening, magnetic separation and eventually a color separation, with the aim of removing impurities such as iron, slag and unwanted pieces of refractory material [2].

The selection and cleaning of these wastes allows the recuperation of metal and the recycling of the majority of the inner part of the spent refractories. This process generates a secondary refractory waste (SRW) composed of the mix of the outer fraction of spent refractory, contaminated with slag and steel as well as with dust particles generated during inner and outer fractions crushing and handling. Nowadays, the recycled fraction is used for the production of new refractories while the secondary wastes lack any effective valorization ways. A possibility for its

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Table 1

Chemical composition, reactivity and mineralogy of the spent refractory materials and binder constituents.

Chemical composition (X-ray Fluorescence)				
%	P1	P2	PC-8	GGBS
SiO ₂	2.07	16.53	2.80	32.18
CaO	3.49	12.51	9.10	43.94
Fe ₂ O ₃	1.16	10.99	2.34	0.33
Al ₂ O ₃	2.81	13.69	0.57	10.40
SO ₃	0.16	0.31	6.27	2.00
Cr ₂ O ₃	0.04	0.43	–	–
P ₂ O ₅	0.14	0.09	–	–
MnO	0.00	1.95	–	–
MgO	76.13	41.11	59.67	0.25
Reactivity				
L.I. 1050 °C (%)	14.00	1.86	19.25	0.46
Free lime (%)	0.84	–	1.32	0.28
Reactivity (min)	>1200	>1200	>1416	>480
pH	11.37	11.69	10.66	9.82

valorization would be the production of artificial aggregates for the construction industry [4]. However, these secondary wastes have limited recyclability as aggregates for construction purposes because of: (i) their small particle size (according to the process usually under 3 mm) and poor mechanical properties which make them unsuitable for replacing fine aggregates, (ii) their free lime (CaO), reactive magnesium oxide (MgO) and calcium silicate (CS) contents, which are associated with deleterious hydration and carbonation processes with expansive effects and volume instability, and (iii) their high pH. These shortcomings for the direct use of the SRW as aggregates could be overcome by means of the waste granulation with a binder, with or without an accelerated carbonation process [5–12]. This way, recycled aggregates with adequate size would be produced, where a binder and CS would hydrate, contributing to the improvement of the aggregates mechanical properties and CaO and MgO could carbonate, creating a denser structure and contributing to the development of mechanical properties.

This article analyzes the ability of SRW for the production of artificial aggregates. A binary hydraulic binder composed of a low-grade magnesium oxide (MgO) and Ground Granulated Blast-furnace Slag (GGBS) was considered. Different binder dosages and CO₂ curing conditions were investigated. A laboratory investigation was carried out to evaluate the aggregates density, granulate size distribution, strength, water absorption and durability with and without accelerated carbonation. Thermo Gravimetric Analysis (TG/DTG) tests were conducted to elucidate the carbonation degree of the treated samples.

2. Materials and methods

2.1. Materials

Two kinds of SRW were considered in this work, named respectively P1 and P2. P1 is generated during the recovery process of refractory bricks from a ladle furnace, while P2 comes from the demolition of a foundry molten steel distribution vessel named “tundish”. Table 1 shows the chemical composition and reactivity parameters of both materials as well as of the magnesium-based binary binder’s constituents (PC-8 + GGBS). Fig. 1 depicts the granulometric curves of all the materials considered in this investigation.

Based on X-ray Diffraction tests P1 mineralogy was estimated mainly as periclase and, to a lower extent, portlandite and CS. P2 contains periclase, monticellite, merwinite, forsterite, magnesioferrite and magnesium iron aluminum oxide. Both refractory wastes could maintain some reactivity that would provoke their instability. This, in addition to their small particle size, makes it necessary for treatment before their use, to be suitable as recycled aggregates for construction.

The binary hydraulic binder was composed of a co-product of low grade MgO, marketed by *Magnesitas Navarras S.A.* Co. under the name PC-8, and GGBS as a source of reactive Si and Al at a ratio of 20 to 80, based on previous experiments [13,14]. PC-8 is a magnesium dust recovered from kilns, where calcined magnesite is produced. This dust contains a mix of unburned magnesite, calcined MgO and eventually sintered MgO, depending on the part of the combustion chamber where they were pulled from and the higher temperature they were exposed to. GGBS is a by-product obtained during the manufacturing of pig iron. It is formed by rapid cooling of molten iron slag to maintain an amorphous structure and ground in order to increase its specific surface area (SSA). The sample available for this investigation was provided by Heidelberg Cement Group (UK). As shown in Table 1, GGBS has a huge cementitious potential due to its richness in reactive calcium, silicon, and aluminum oxides.

2.2. Samples manufacturing

Dry SRW and binder constituents were pre-mixed in a laboratory mixer for 5 min to guarantee a complete homogenization. The waste to binder ratios considered were 90 to 10, 80 to 20 and 70 to 30 [11,15–17]. Once the mix was homogenized, 2 kg were poured in the granulator. It was 600 mm in diameter, 370 mm in collar height and was equipped with a blade. Granulation was performed under laboratory conditions. The revolution speed for granulating was set at 50 rpm with a tilting angle of 15°. Once the granulator had been turned on, 400 g of deionized water were sprayed in the granulator (water to solid ratio of

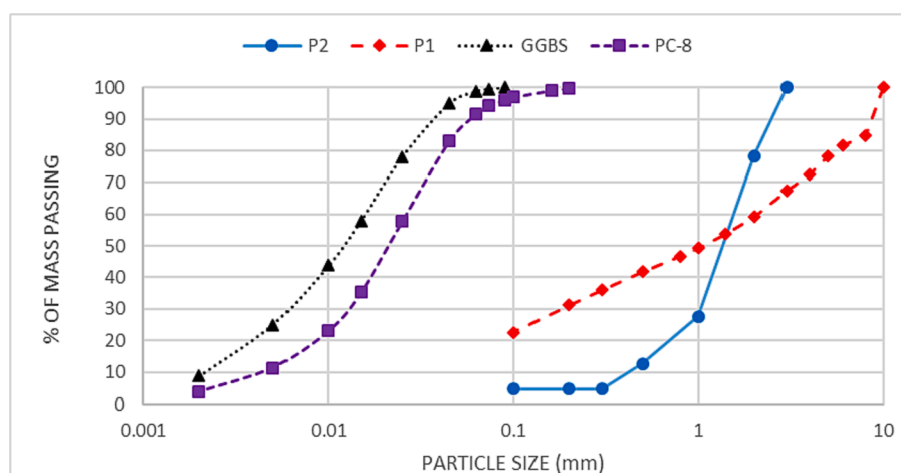


Fig. 1. Granulometric curves of the spent refractory materials and the binder constituents.

Table 2
Granulate combinations manufactured.

COMBINATION	SRW KIND	SRW MASS (g)	BINDER MASS (g)	WATER MASS (g)	CURING TIME (days)	CURING ATMOSPHERE
P1/10/7/A	P1	900	100	200	7	Air
P1/20/7/A	P1	800	200	200	7	
P1/30/7/A	P1	700	300	200	7	
P1/10/28/A	P1	900	100	200	28	
P1/20/28/A	P1	800	200	200	28	
P1/30/28/A	P1	700	300	200	28	
P1/10/7/C20	P1	900	100	200	7	CO ₂ 20 % N ₂ 80 %
P1/20/7/ C20	P1	800	200	200	7	
P1/30/7/ C20	P1	700	300	200	7	
P1/10/28/ C20	P1	900	100	200	28	
P1/20/28/ C20	P1	800	200	200	28	
P1/30/28/ C20	P1	700	300	200	28	
P1/10/7/C100	P1	900	100	200	7	CO ₂ 100 %
P1/20/7/ C100	P1	800	200	200	7	
P1/30/7/ C100	P1	700	300	200	7	
P1/10/28/ C100	P1	900	100	200	28	
P1/20/28/ C100	P1	800	200	200	28	
P1/30/28/ C100	P1	700	300	200	28	
P2/10/7/A	P2	900	100	200	7	Air
P2/20/7/A	P2	800	200	200	7	
P2/30/7/A	P2	700	300	200	7	
P2/10/28/A	P2	900	100	200	28	
P2/20/28/A	P2	800	200	200	28	
P2/30/28/A	P2	700	300	200	28	
P2/10/7/C20	P2	900	100	200	7	CO ₂ 20 % N ₂ 80 %
P2/20/7/ C20	P2	800	200	200	7	
P2/30/7/ C20	P2	700	300	200	7	
P2/10/28/ C20	P2	900	100	200	28	
P2/20/28/ C20	P2	800	200	200	28	
P2/30/28/ C20	P2	700	300	200	28	
P2/10/7/C100	P2	900	100	200	7	CO ₂ 100 %
P2/20/7/ C100	P2	800	200	200	7	
P2/30/7/ C100	P2	700	300	200	7	
P2/10/28/ C100	P2	900	100	200	28	
P2/20/28/ C100	P2	800	200	200	28	
P2/30/28/ C100	P2	700	300	200	28	

0.2) during one minute, and granulation continued for 10 min to complete the granulates formation process [18]. This procedure was repeated three times for each combination, to obtain the necessary amount of granulates. Afterwards, granulates were collected and cured in natural air atmosphere, as well as in atmospheres composed of 20 % CO₂ and 80 % N₂, and in 100 % CO₂, until the testing ages of 7 and 28

days. Before testing, samples were dried at 105 °C for 24 h. A total of 36 combinations were manufactured. Each combination was designated by the code SRW/BP/CT/CA being:

SRW waste type (P1, P2).

BP binder percentage (10 %, 20 %, 30 %).

CT curing time (7 days, 28 days).



Fig. 2. Appearance of manufactured granulates.

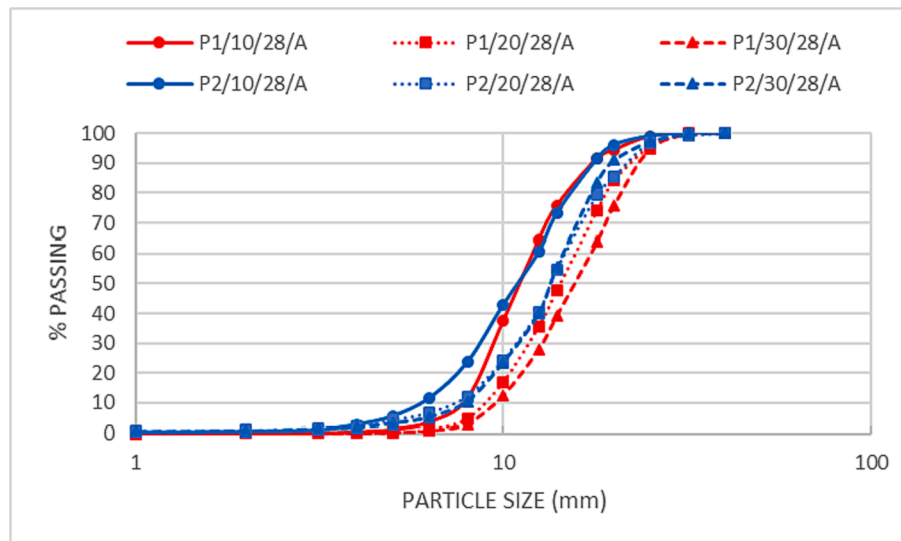


Fig. 3. Granulometric curves of the granulates manufactured.

CA curing atmosphere (air, CO₂ 20 %, CO₂ 100 %).

Table 2 shows the combinations produced, their composition and the curing atmosphere.

2.3. Samples testing

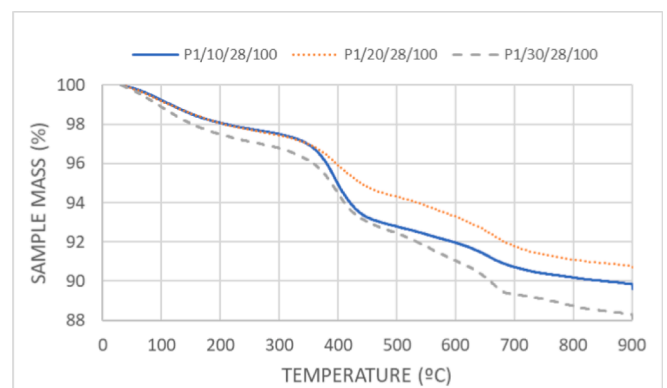
Granulate particles size distribution was obtained through sieving test with square-opening sieves in accordance with the standard EN 933-1. TG/DTG tests were used to analyze the chemical composition within decomposition of samples against temperature. This test was carried out with 30 mg of sample from 25 °C to 900 °C in nitrogen atmosphere with a flux rate of 100 ml/minute. Bulk density was determined in accordance with the standard UNE-EN 1097-3, eliminating particles bigger than 20 mm. Particle density and water absorption were determined in accordance with the standard UNE-EN 1097-6, through the hydrostatic weighing method. Particle sizes smaller than 4 mm and >20 mm were not considered in this test. Granulate strength was measured using the single pellet crushing method [11]. 40 granulates of 14–18 mm diameter of each combination were used for this test. The fracture load of each single granulate was calculated according to the standard ISO 8942. The samples mechanical strengths were obtained as the mean value of dividing the fracture loads by the granulate areas at the maximum diameter section.

3. Results and discussion

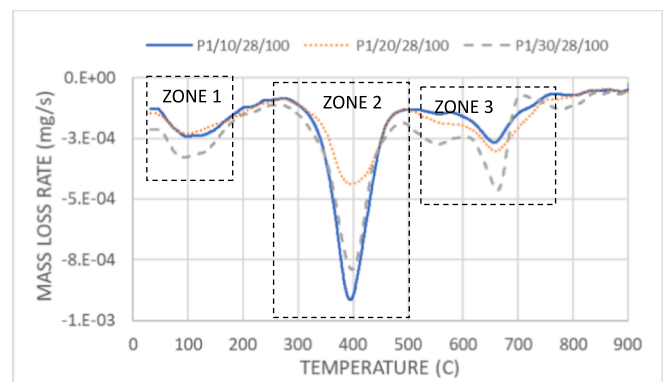
3.1. Granulates particle size distribution

Fig. 2 shows the granulates appearance after manufacturing. Fig. 3 depicts the aggregates granulometric particles size distribution of the air cured combinations at the age of 28 days.

As expected, granulates were mostly spherical, demonstrating that the considered granulation time was enough to complete the layering over the agglomeration process [12]. All the combinations showed continuously graded granulometric curves with >95 % of the granulate sizes in the range 3.15/25 mm, in accordance with other authors like Azrar et al. [19]. The relation between the granulate maximum and minimum diameters is in all the combinations >1.4 ($D/d \geq 1.4$), accomplishing the requirements of the Spanish standard for structural concrete EHE08. For both SRW wastes, granulates diameter increased as the binder content did: P2/10/28/A reached the finest granulate sizes and P1/30/28/A the coarsest ones, demonstrating the effect of the binder dosage in the granulates size distribution and the ability of P1 to



a)



b)

Fig. 4. Decomposition curves against temperature of P1 samples at 28 days, with 10 %, 20 % and 30 % of binder dosage, cured in 100 % CO₂ atmosphere. a) TG curves, b) DTG curves.

produce aggregates with greater diameter than P2.

3.2. Chemical composition

TG/DTG tests were carried out to analyze chemical composition of the granulates within their decomposition of samples against

Table 3

Percentages of mass losses for each combination related to the dehydration, dehydroxylation and decarbonation processes.

COMBINATION	ZONE 1 DEHYDRATION (50 °C-200 °C)	ZONE 2 DEHYDROXYLATION (250 °C-500 °C)	ZONE 3 DECARBONATION (500 °C-750 °C)
	% of total mass	% of total mass	% of total mass
P1/10/7/A	0.00	2.29	2.14
P1/20/7/A	1.27	2.34	2.82
P1/30/7/A	1.64	3.42	3.42
P1/10/28/A	1.00	2.27	2.09
P1/20/28/A	1.23	2.25	2.76
P1/30/28/A	1.41	2.34	3.37
P1/10/7/C20	1.15	2.66	2.31
P1/20/7/C20	1.75	3.82	2.57
P1/30/7/C20	1.72	2.60	2.93
P1/10/28/C20	1.41	3.18	2.58
P1/20/28/C20	1.81	3.32	3.12
P1/30/28/C20	1.83	3.05	3.26
P1/10/7/C100	2.14	5.32	2.41
P1/20/7/C100	2.03	4.77	2.77
P1/30/7/C100	2.39	4.96	3.07
P1/10/28/C100	1.79	4.97	2.39
P1/20/28/C100	1.78	3.40	2.96
P1/30/28/C100	2.26	4.67	3.36
P2/10/7/A	0.51	0.56	1.35
P2/20/7/A	0.85	1.03	1.99
P2/30/7/A	0.83	1.10	2.31
P2/10/28/A	0.58	0.59	1.44
P2/20/28/A	0.77	1.01	1.97
P2/30/28/A	1.04	1.28	2.39
P2/10/7/C20	0.65	0.73	1.44
P2/20/7/ C20	1.12	1.30	2.06
P2/30/7/C20	1.20	1.45	2.70
P2/10/28/C20	1.00	1.15	1.78
P2/20/28/C20	1.28	1.47	2.05
P2/30/28/C20	1.46	1.66	3.04
P2/10/7/C100	1.94	3.96	2.44
P2/20/7/C100	1.40	2.25	2.24
P2/30/7/C100	1.72	2.75	2.59
P2/10/28/C100	1.45	2.32	2.75
P2/20/28/C100	2.22	4.20	3.14
P2/30/28/C100	2.08	3.36	3.52

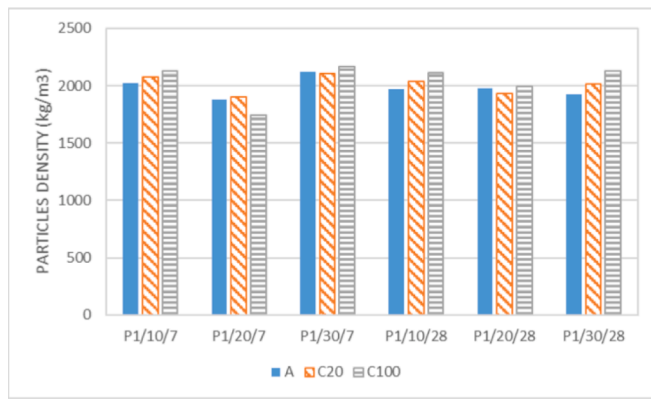
temperature. TG curves showed the mass loss at the different temperature ranges (Fig. 4a). DTG curves (Fig. 4b) were used to identify the ranges of temperatures at which dehydration, dehydroxylation and decarbonation processes occur [20]. Fig. 4 shows as an example the TG/DTG curves of P1 samples at 28 days, with 10 %, 20 % and 30 % of binder dosage, cured in 100 % CO₂ atmosphere.

The three decomposition characteristic zones of the cementitious products were observed in DTG curves [21,22]. In this investigation zone 1 ranged between 50 °C and 200 °C, corresponding to the loss of free water and water physically adsorbed in hydration products like CSH and MSH gels [12,21,22], which therefore corresponds to the dehydration zone. Zone 2 comprised the temperature range between 250 °C and 500 °C. This region corresponded to the dehydroxylation of Ca(OH)₂ and Mg(OH)₂ [8,12,23,24]. The third decomposition zone was identified in the range between 500 °C and 750 °C [12,20,25,26] as decarbonation zone. The main peak of this zone, due to the decomposition of calcium carbonates CaCO₃, was centered at about 650 °C. Fig. 4b shows how a secondary peak centered at about 550 °C appeared in zone 3, more clearly for the dosage of 30 %. This result was attributed to the decomposition of magnesium carbonate MgCO₃.

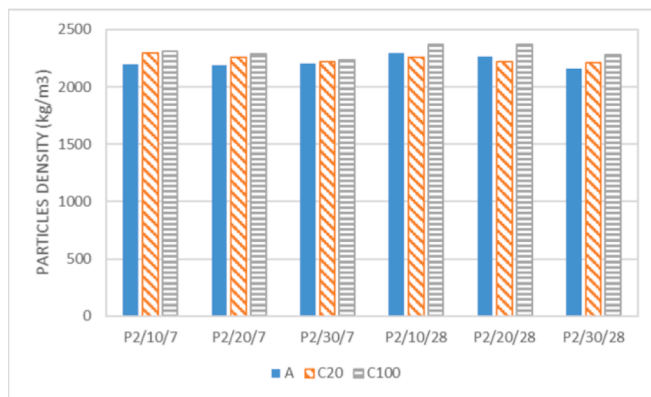
Table 3 shows the percentages of mass losses for each combination obtained in the TG curves related to the dehydration, dehydroxylation and decarbonation processes previously defined from the TG/DTG test.

TG/DTG test results showed some interesting trends among samples that highlight the differences between the SRW kind, binder dosage, curing atmosphere and curing time. Keeping the other variables constant, P2 combinations showed in general lower loss of mass related to the dehydration, dehydroxylation and decarbonation processes

compared to P1. This could be related to the lower MgO content of this SRW, 41.11 %, compared to P1 with 76.13 %, that would maintain some reactivity and ability to hydrate, to create cementitious gels and to carbonate in presence of CO₂. As expected, for both SRW, hydration degree increased as the binder content did. No significant increase in hydration degree trends were observed from 7 to 28 days, revealing a rapid cementitious gels formation from the MgO of the binder that was completed before 7 days and a very low reactivity of the MgO (as periclase) from the SRW [23]. A direct relationship between the CO₂ content of the curing atmosphere and the hydration degree was observed. This suggests a positive effect of CO₂ curing for the cementitious gels formation and contradicts the results of Unluer and Al-Tabbaa [8] who observed that CO₂ curing consumed MgO for carbonation making it not available for the GGBS activation. Dehydroxylation did not show a direct relationship with the binder content, but a positive effect of the curing under 100 % CO₂ atmosphere on the dehydroxylation was observed. This showed that this curing method favored the formation of portlandite and brucite from the SRW while the CaO and MgO from the binder were probably spent for the cementitious gels formation at the earlier ages of the curing period. This effect was more intense in the P2 combinations and would be attributed to the highest content of CaO of this waste compared to P1. Direct relationships between the binder dosage and the decarbonation intensity, as well as between the curing time and the decarbonation intensity were observed for both SRW. P1 combinations did not show any relationships between the curing atmosphere and the carbonation degree as previously observed by Kim et al. [11], with the main decarbonation peak being attributed to the calcium carbonates decomposition [25]. As previously commented,



a)



b)

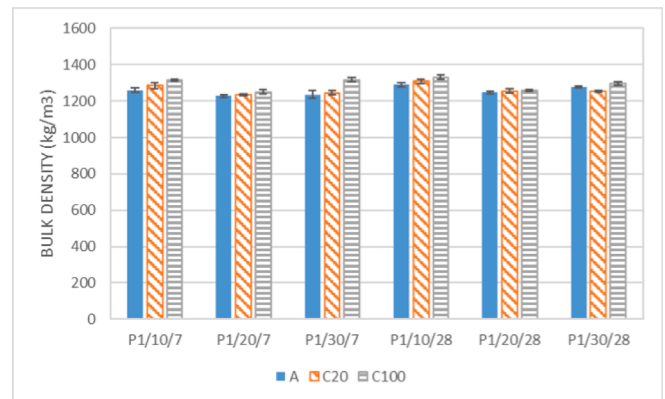
Fig. 5. Particle densities of the aggregates manufactured in function of the atmosphere curing. a) P1 combinations and b) P2 combinations.

these combinations also showed a secondary peak in the carbonation zone of the DTG curves centered at the 550 °C, attributed to magnesium carbonates decomposition [23]. P2 combinations showed a direct relationship between the carbonation degree and the binder dosage as well as between the carbonation degree and the CO₂ content of the curing atmosphere. The peak at 550 °C was not clearly observed in the P2 combinations. These results suggest that an important amount of the decarbonation was due to the carbonates content of the PC-8 because of its manufacturing process [27]. The presence of the magnesium carbonate peak in the P1 samples, directly related to the binder content, independently of the curing atmosphere, suggests an origin of these carbonates from the binder. At the same curing ages and with the same binder dosages, P2 combinations showed higher contents of carbonates than P1 ones. Carbonation degree increased from 7 days to 28 days. A direct relationship between the curing atmosphere CO₂ content and carbonation mass loss was also observed. This revealed the higher ability of P2 combinations to uptake CO₂ and to produce calcium carbonates during the curing period.

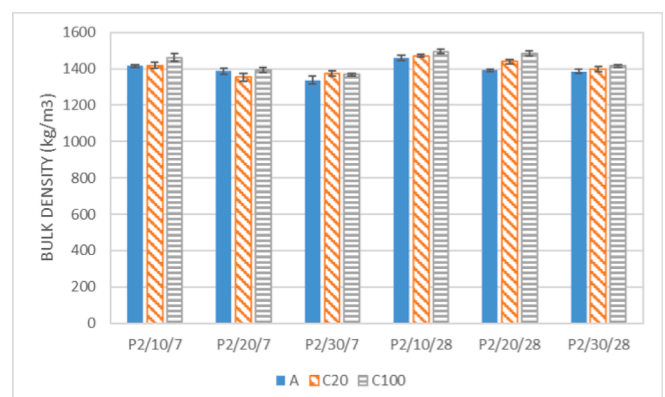
3.3. Granulates physical properties

Figs. 5 and 6 show the particle densities and the bulk densities of the manufactured granulates at the ages of 7 and 28 days.

All the combinations reached relatively low values of particle densities and bulk densities compared to natural aggregates but in accordance with those obtained by Jiang and Ling [12] from steel-making slag granulation. P2 combinations showed higher particle densities and bulk densities compared to P1 ones. These differences were attributed to the coarser granulometry of the P2 and its higher content of iron oxide,



a)



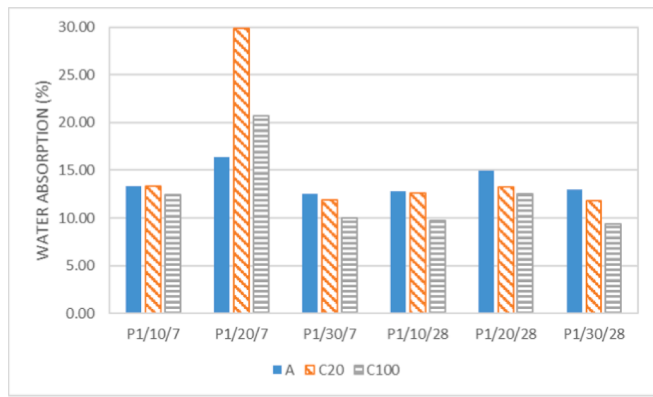
b)

Fig. 6. Bulk densities of the aggregates manufactured of atmosphere curing. a) P1 combinations and b) P2 combinations.

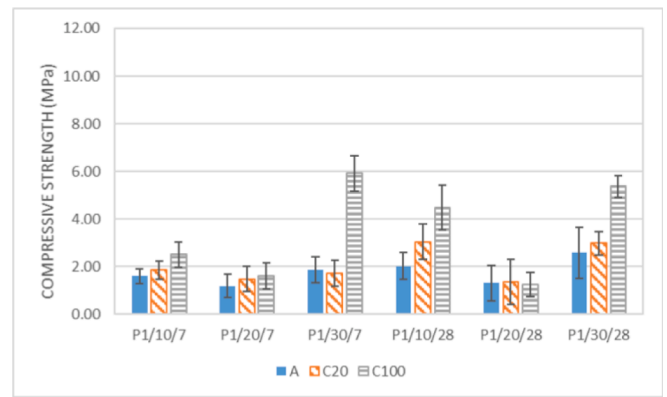
compared to P1.

The P1 particle densities oscillated between 1,740 kg/m³ and 2,160 kg/m³, corresponding to the combinations P1/20/7/100 and P1/30/7/100, respectively. No significant relationships were observed between particle density and binder dosage or curing age. Only a slight increase of the particle densities in the CO₂ curing atmospheres was observed. This fact could be attributed to the granulates manufacturing inhomogeneities, testing uncertainties, close particle densities achieved by the different samples, or overlapping effects of hydration and carbonation processes [11,12,16,25]. P2 particle densities oscillated in the range 2,160–2,370 kg/m³, reached by the combinations P2/30/28/A and P2/20/28/100, respectively. P2 combinations achieved higher particle densities than P1 ones, probably based on the lower fine particles content or on the chemical composition of P2. Despite some inconsistent results that were attributed to the same reasons than in the case of the P1 combinations, P2 samples showed an indirect correlation between the particle density and the binder dosage. A direct relationship between the particle density and the curing CO₂ concentration was also observed.

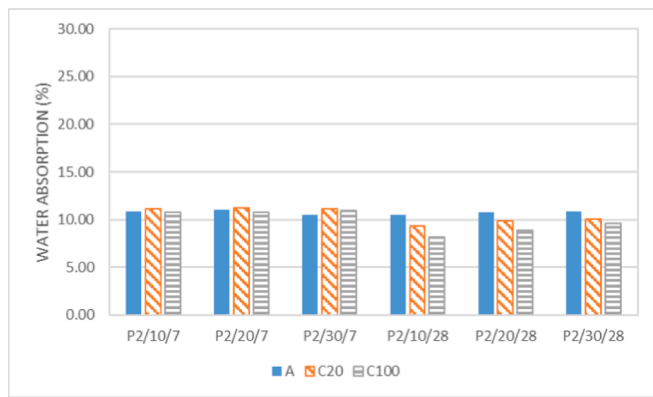
P1 bulk densities oscillated between 1,230 kg/m³ and 1,330 kg/m³, reached by the combinations P1/20/7/A and P1/10/28/100 respectively. Direct relationships between the bulk density, the curing time and the CO₂ concentration of the curing atmosphere were observed. This effect was attributed to the carbonation process that would create a denser micro-structure, as observed by Mo and Panesar [25], Shi Ling y Guo [17] and Jiang y Ling [12]. Kim et al. [11] determined that an atmosphere containing a CO₂ concentration of 20 % was the optimum to get the densest and strongest carbonated MgO-GGBS structure. Tam et al. [28] observed an increase of the porosity and a decrease of the



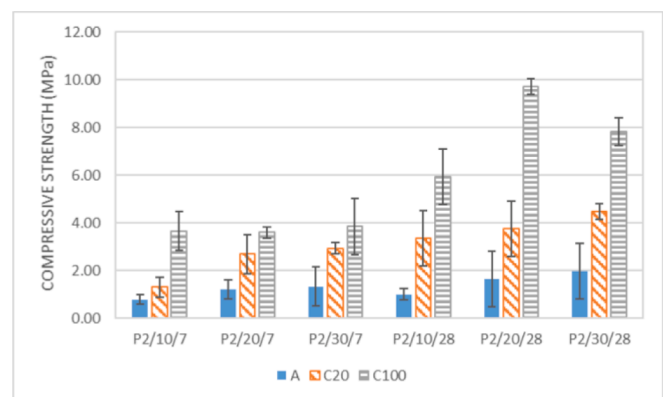
a)



a)



b)



b)

Fig. 7. Water absorption of the granulates manufactured. a) P1 combinations and b) P2 combinations.

strength of cement pastes due to carbonation. These contradictory results highlight the complexity of the effect of the binder hydration and carbonation. Both processes occur simultaneously in the CO₂ curing of granulates and the differences of materials used, manufacturing and curing conditions would justify the variability of the results achieved in different studies. An indirect relationship between the bulk density and the binder content was identified and it was attributed to the content of coarser particles of P2. Thus, P2 samples reached a minimum bulk density of 1,340 kg/m³ corresponding to the combination P2/30/7/A, containing the highest binder proportion and cured in air. On the other hand, the maximum bulk density, 1,50 kg/m³, was achieved by the combination P2/10/28/100, containing the lowest binder dosage, an atmosphere of 100 % CO₂ and the longest curing time.

These particle densities and bulk densities results show that combinations P1/10/28/A, P1/20/28/A, P1/20/28/C20, P1/20/28/C100 and P1/30/28/A fulfilled the requirement of particle density lower than 2000 kg/m³ set in the standard EN 13055-1 to be considered lightweight aggregates for concrete, mortar and grout. Fig. 7 depicts the water absorption test results of the granulate combinations at the different curing ages.

P1 combinations achieved water absorptions in general between 9 % and 15 %. Only P1/20/7 combinations showed a different behavior with water absorptions between 16 % and 30 %. On the other hand, P2 combinations water absorptions oscillated between 8 % and 11 %. In general, a correlation between the decrease of the water absorption, the curing time and the CO₂ concentration was observed. These results agree with those obtained by Shi et al. [29] and were attributed to the reduction of porosity in the aggregates matrix due to the binder carbonation.

Fig. 8. Compressive strength test results of the granulates manufactured. a) P1 combinations and b) P2 combinations.

3.4. Granulates mechanical properties

Fig. 8 shows the compressive strength of the granulates manufactured.

Compressive strength oscillated between 0.79 MPa and 9.71 MPa, corresponding to the combinations P2/10/7/A and P2/20/28/100. These results agree with those obtained by other authors and are adequate for the substitution of natural aggregates in construction and environmental applications [11,12,15,17]. Carbonation showed a beneficial effect on the granulates compressive strength, more clearly for P2 combinations, mainly when curing was carried out in 100 % CO₂ atmosphere. Unexpectedly, P1 combinations did not show any direct relationship between the compressive strength and the binder content at any curing age or curing condition. Thus, for example, the combinations P1/10/28/20, P1/20/28/20 and P1/30/28/20, reached respectively mean compressive strengths of 3.04 MPa, 1.34 MPa and 2.97 MPa. The same was observed related to the curing time with no clear compressive strengths increase patterns from 7 to 28 days. Among the P1 combinations, the best compressive strengths were achieved by the combinations P1/30/7/100, with 5.92 MPa, P1/30/28/100, with 5.37 MPa and P1/10/28/100, with 4.48 MPa. Despite the uncertainties of the results, a decrease of the compressive strength seems to occur between the age of 7 days and 28 days in P1 samples cured in 100 % CO₂ atmosphere. It could be due to the formation of magnesium carbonates with a relatively weak structure or to the formation of expansive minerals that hinder the granulates strength [11]. P2 samples showed more predictable general behavior trends. Compressive strengths increased as the binder content did. For the same binder content, at the same curing age, compressive strength increased as the CO₂ concentration did. From 7 to 28 days, air

cured samples compressive strengths remained steady. On the other hand, for granulates cured in a CO₂ atmosphere the compressive strengths increased, mainly for the samples cured in 100 % CO₂ atmosphere. This demonstrates the beneficial effect of the carbonation of the granulates for their mechanical strength development.

4. Conclusions

This work analyzes the ability of two SRW with a binary MgO-GGBS hydraulic binder for the manufacturing of recycled granulates. Both SRW varieties demonstrated their potential to be used as target materials for producing granulates that accomplish the requirements for construction and environmental applications. SRW showed a residual reactivity that could benefit the manufacturing of recycled aggregates with improved properties. The empirical investigation carried out demonstrated the effectiveness of CO₂ curing conditions for the formation of cementitious gels and for the increase granulates carbonation degree that contributed to the reduction of the water absorption and to the increasing of the granulates compressive strength. Negative strength developments due to the formation of magnesium carbonate were not observed. Although the beneficial effects of the curing in CO₂ atmospheres were observed in the combinations of both SRW, their intensity was different based on their composition differences and reactivity. This highlights the complexity of processes that overlap in the granulates strength development like cementation and carbonation. More investigations are required to get a better knowledge of the cementation and carbonation processes interaction in SRW granulates curing under different atmospheres.

Granulation process uncertainties also would require further analysis as potential source of granulate inhomogeneities. These manufacturing inhomogeneities probably were responsible of some unexpected results that contradicted the general trends observed in results obtained in this experimental investigation.

CRedit authorship contribution statement

A. Seco: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **J.M. del Castillo:** Methodology, Formal analysis, Investigation, Writing – original draft. **C. Perlot:** Investigation, Formal analysis, Writing – review & editing. **S. Marcelino:** Resources, Investigation, Visualization, Project administration. **S. Espuelas:** Investigation, Data curation, Formal analysis, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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ARTÍCULO 3

Article

Stabilization of a Clay Soil Using Cementing Material from Spent Refractories and Ground-Granulated Blast Furnace Slag

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Abstract: Nowadays, huge amounts of refractory materials are generated around the world. The majority of them lack valorization methods. This study analyzes the ability of a doloma and two magnesia spent refractory wastes as soil stabilizers on their own, as well as when combined with Ground-Granulated Blast Furnace Slags (GGBS). These materials showed a limited ability for the soil's plasticity modification from a plasticity index of 15.6 to a minimum of 12.7. The high pH of the additives increased the soil's pH from 7.88 to values in the range of 10.94–11.25 before the 28 days, allowing the development of the pozzolanic reactions. Unconfined compressive strength (UCS) increased along the curing time, reaching a maximum value of 5.68 MPa after 90 days. Based on the UCS, the optimum refractory GGBS ratios oscillate between 30:70 and 50:50. The UCS values after soaking samples reduced the unsoaked results between 68.70% to 94.41%. The binders considered showed a low effect against the soil swelling and the lack of delayed expansive effects because of the MgO hydration. Finally, X Ray Diffraction (XRD) tests showed that the stabilization only slightly modified the combinations of mineralogy and the formation of Magnesium Silicate Hydrate (MSH) gels.

Keywords: spent refractory materials; waste valorization; soil stabilization; binders; sustainable construction



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1. Introduction

Stabilization is an effective way to increase the bearing capacity of soft soils. The term stabilization usually refers to the addition of chemical admixtures for the geotechnical soil enhancement. Among them, calcium-based additives like lime or cement, used on their own or combined with other substances, are nowadays the most common binders [1]. Khazaei and Moayedi [2] analyzed the improvement of the properties of an expansive soil stabilized with waste from a petrochemical plant and quick lime. They observed the improvement of the bearing capacity of the treated soil samples. Okeke [3] studied the engineering behavior of an expansive soil stabilized with lime and waste ceramic dust. They observed the early strength development that occurred in the soils mixed with lime and the ceramic waste and the decrease in the soil plasticity index. Hozatlıoğlu and Yılmaz [4] stated the improvement of lime compared to fly ash and gypsum on the stabilization of swelling soils. Baldovino et al. [5] stated the improvement in the microstructure and mechanical properties of a soil treated with dolomitic lime and recycled-glass powder. Chenarboni et al. [6] investigated the effect of different percentages of cement and zeolite for the stabilization of an expansive soil. They found that the substitution of 30% of cement by zeolite reached the highest unconfined compressive strength (UCS) results.

Soil stabilization requires huge amounts of cement and lime whose manufacturing processes generate high environmental impacts in terms of raw materials consumption,

energy spending and CO₂ emissions [7]. A possible alternative to the calcium-based soil stabilizers are the magnesium-based ones. Magnesium-based binders have demonstrated in recent years to be effective and more sustainable alternatives to lime and to cement. Yi et al. [8] stabilized two clayey soils with binders based on reactive MgO and Ground-Granulated Blast Furnace Slag (GGBS). They found that the optimum UCS were obtained with binary MgO-GGBS binders whose ratios were generally in the range of 19:1–4:1. At the age of 28 days, these binders reached UCS values that exceeded the cement results by 1.3–4 times. Seco et al. [9] stabilized five soils containing sulfates with a low-grade MgO on its own at first, and then combined it with GGBS. They demonstrated the ability of the low-grade MgO for diminishing the soils' swelling, and its convenience for the five soils' stabilization and for the activation of GGBS. Li et al. [10] investigated the stabilization of a gypseous soil with binders based on high-grade and low-grade MgO products, combined with GGBS at different ratios. They stated the convenience of the MgO-GGBS binary binders for the stabilization of their gypseous soil and the better efficiency of the high-grade MgO compared to the low-grade MgO for the GGBS activation. The lower environmental impact of the magnesium-based binders is due to two main factors: (i) The lower manufacturing temperature of the MgO compared to the one of the calcium-based additives, and (ii) the use of recycled sources of reactive silicon and aluminum like GGBS or pulverized fuel ash [11]. Despite its demonstrated technical convenience and its higher sustainability compared to lime and cement, reactive MgO manufacturing shows some drawbacks: (i) Its production consumes magnesite rock, which is a scarce material [12], (ii) its manufacturing is based on the magnesite decarbonation that consumes huge amounts of energy and releases CO₂ [8] and (iii) calcined magnesite is an expensive material, making the use of MgO uneconomical compared to lime or cement [13]. These reasons make the discovery of new economical and more environmentally friendly sources of reactive MgO for the soils' stabilization necessary.

In the European Union (EU), the production of spent refractories is estimated between 1.42 and 2.66 million tons per year. Although many efforts are being conducted, these debris are an economic and environmental concern as they lack effective ways of valorizing the huge volumes generated [14–16]. Of these wastes, 26% are doloma and magnesia recycled refractory materials (DMRR) from the steel industry [17]. This is a potential availability of 0.43 to 0.80 million tons per year only in the EU. DMRR could become constituents for the production of MgO binders based on their high pH and their reactive MgO, free lime (CaO) and dicalcium silicate (C₂S) contents [17,18].


The objective of this work is to state the ability of spent refractory wastes as constituents of sustainable binary hydraulic binders for the stabilization of clayey soils. These materials could become recycled sources of reactive MgO and CaO that could replace commercial additives like lime or calcined magnesia. Thus, soils' stabilization would become an effective way for the valorization of the huge amounts of spent refractories generated around the world, contributing to decrease the environmental impact of the soils' stabilization. Thus, this article analyzes the ability of three kinds of spent refractories, on their own as well as when combined with GGBS at different ratios, for the stabilization of a clayey soil. A laboratory investigation was carried out to analyze the effect of the DMRR considered in a clayey soil as well as their ability for the activation of GGBS. The potential of these binders was evaluated by means of the analysis of the physical, mechanical and chemical properties of soil samples stabilized with these binders.

2. Materials and Methods

2.1. Materials

The soil used in this investigation was a sample of clay, collected in Pamplona (Spain). This clay soil is generated by in situ weathering processes of the local Tertiary marly rock. In order to carry out this experiment, one ton of clay was extracted, and, after homogenization of the sample, it was air-dried, crushed and sieved to a maximum particle size of 2 mm. Table 1 contains the characterization of the soil sample considered.

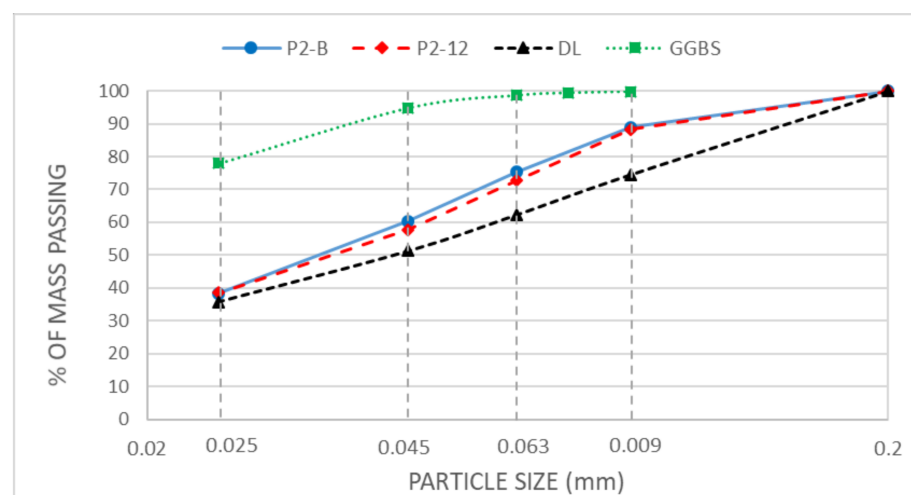
Table 1. Characterization of the soil sample.

Extraction Coordinates		
X: 612.110 Y: 4.740.296 (UTM 30 ETRS89):		
Soil Mechanic Properties	Chemical Properties	
Atterberg limits (UNE 17892-12) [19]:	Organic matter (UNE 103204) [20]: 0.32%	
Liquid Limit: 38.4%	Soluble sulfates (EN 1744-1) [21]: 0.05%	
Plastic Limit: 22.8%	pH in water: 7.88	
Plasticity Index: 15.6%	Mineralogy (X-ray diffraction):	
Standard Proctor (UNE 103500) [22]:	Calcite	
Maximum density: 1.76 g/cm ³	Quartz	
Optimum moisture content: 18.5%	Halloysite	
Unified Soil Classification: CL	Albite	
Unconfined Compression Strength (UNE 17892-7) [23]:	Chemical composition (X-ray fluorescence):	
Before soaking: 0.619 MPa	Element:	%
After soaking: 0.000 MPa	Ca	50.41
Free Swelling (UNE 103601) [24]: 0.5%	Si	23.92
California Bearing Ratio index (UNE 103502) [25]: 2.44	Al	10.81
	Fe	7.78
	K	3.39
	Mg	1.92
	S	0.09
Color		
(based on the Munsell Soil Color Chart):		
10YR 7/4		
		

Three types of DMRR were considered in this work: Two magnesia refractory wastes named P2B and P2-12 respectively, and a doloma refractory waste named doloma lime (DL). Both P2 wastes come from the demolition of tundishes of a steel foundry: P2B is the denomination of the material recovered from the outer part of the refractory covering. This fraction is in contact with the molten metal and the slag. This fact modifies its chemical composition and sinters the refractory material that is recovered in the form of big blocks after the tundish demolition. P2-12 is the inner part of the spent magnesia refractory that is recovered in dust form. As this material is not in contact with the molten metal or the slag, it maintains a chemical composition close to that of the raw refractory. DL is made of the spent refractory of ladle furnaces. It shows higher CaO and SO₃ contents than P2 wastes due to its direct contact with the ladle slag. The DMRR samples considered in this investigation were ground to reduce their granulometry and increase their surface-specific area. GGBS is a byproduct obtained during the manufacturing of pig iron. It has a large pozzolanic activity as a result of its richness in reactive calcium, silicon and aluminum oxides. GGBS is formed by rapid water cooling of molten iron slag that maintains an amorphous structure. After cooling, GGBS is dried and then ground to increase its specific surface area and thus increase its reactivity. Table 2 shows the chemical composition and reactivity parameters of these wastes. Figure 1 depicts the ground granulometric curves of the DMRRs used in this investigation.

Table 2. Chemical composition and reactivity parameters of the doloma and magnesia recycled refractory materials (DMRRs) and the Ground-Granulated Blast Furnace Slags (GGBS) samples.

Chemical Composition (X-ray Fluorescence)				
%	P2B	P2-12	DL	GGBS
SiO ₂	12.45	10.53	12.38	32.18
CaO	10.89	9.8	29.37	43.94
Fe ₂ O ₃	12.13	3.31	2.54	0.33
Al ₂ O ₃	6.51	5.32	5.53	10.40
SO ₃	0.36	0.32	1.17	2.00
Cr ₂ O ₃	0.42	0.1	0.08	-
P ₂ O ₅	0.11	0.06	0.13	-
MnO	0.26	-	0.00	-
MgO	53.75	63.55	42.88	0.25
Reactivity				
Loss of ignition at 1050 °C	6.02	4.26	5.91	0.46
Free lime (%)	0.60	0.71	3.69	0.28
Reactivity (min)	>240 min	>240 min	>240 min	>480 min
pH in water	11.62	11.73	12.07	9.54

**Figure 1.** Granulometric curves of the DMRRs and GGBS samples used in this investigation.

2.2. Samples' Manufacturing and Testing

The samples' manufacturing was carried out as follows: dried soil and additives were mixed together in a laboratory mixer for 5 min. After that, water corresponding to the optimum moisture of the soil, in accordance with the Standard Proctor (SP) test, was added slowly. An additional wet mixing was carried out for 5 min to guarantee a complete homogenization of the soil, additives and water. Once the quality of each mixture was verified visually, samples were collected for pH and Atterberg limits tests. Specimen pH values were determined according to the standard UNE-ISO 10390 by using a laboratory pH meter with an accuracy of ± 0.01 . Atterberg limits were stated based on the Spanish Standards UNE 103103 (Liquid Limit) and UNE 103104 (Plastic Limit). The samples' Plasticity Index (PI) was defined as the difference between Liquid and Plastic Limits.

For the mechanical strength testing, cylindrical samples of 65 mm in diameter were prepared: 450 g of the wet mixes were pressed to 1.5 MPa into a mold, at a constant velocity of 50 mm/min. This was the pressure required to get the SP maximum density. Once compacted, samples were immediately demolded and wrapped in a polyethylene sheet in order to avoid dehydration. Specimens were cured in a wet chamber at 20 °C and 100% of relative humidity to the testing ages of 7, 28, 56 and 90 days. The mechanical properties

of the samples were characterized according to the UCS test as defined in the Spanish standard UNE 103400. The UCS tests were conducted at the ages of 56 and 90 days, with two sets of samples: one without any conditioning of the curing ages, and the other after 24 h of moisture conditioning, as defined in Li et al. [10]. After testing, representative fragments of the specimens were crushed and used for the determination of the cured samples' pH values as previously defined. At the ages of 28 and 90 days, sample fragments were crushed and dried for 1 week at 40 °C in a desiccator with silica gel and a CO₂ sorbent. This conditioning was carried out to completely stop the cementation reactions. Fifty grams of each combination were ground and homogenized prior to the X-ray diffraction (XRD) analysis of these samples. A swell strain test after prolonged exposure to moisture was carried out to prevent any expansive effect of the treated soil samples. For this test, after the combinations' mixing, samples of 63 mm in diameter and 20 mm in height were prepared at SP test maximum density and optimum moisture content, inside oedometer sample rings. The mixing as well as the sample compaction were performed manually, in accordance with the Spanish standard UNE 103601. Samples were maintained in water immersion for 15 days and linear expansion was registered daily by means of dial gauges with an accuracy of 10⁻⁵ m. Table 3 shows the 13 combinations of soil and additives considered for the experimental investigation.

Table 3. Soil and additive combinations considered in the laboratory investigation.

COMBINATION	CODE	SOIL	P2-B	P2-12	DL	GGBS
SOIL	SOIL	100				
SOIL + P2B	P2-B (100/0)	95	5			
SOIL + P2-12	P2-12 (100/0)	95		5		
SOIL + DL	DL (100/0)	95			5	
SOIL + GGBS	GGBS	95				5
SOIL + P2B + GGBS (30/70)	P2-B (30/70)	95	1.5			3.5
SOIL + P2B + GGBS (50/50)	P2-B (50/50)	95	2.5			2.5
SOIL + P2B + GGBS (70/30)	P2-B (70/30)	95	3.5			1.5
SOIL + P2-12 + GGBS (30/70)	P2-12 (30/70)	95		1.5		3.5
SOIL + P2-12 + GGBS (50/50)	P2-12 (50/50)	95		2.5		2.5
SOIL + P2-12 + GGBS (70/30)	P2-12 (70/30)	95		3.5		1.5
SOIL + DL + GGBS (30/70)	DL (30/70)	95			1.5	3.5
SOIL + DL + GGBS (50/50)	DL (50/50)	95			2.5	2.5
SOIL + DL + GGBS (70/30)	DL (70/30)	95			3.5	1.5

In Table 3, samples constituents are expressed as percentages of dry mass, considering total dosages of 5%.

3. Results and Discussion

3.1. Soil Plasticity

Table 4 shows the Atterberg limits and Plasticity Index of the combinations considered in the laboratory investigation.

When P2B, P2-12, DL and GGBS were added, the LL of the soil decreased from 38.4 to 34.2, 36.1, 38.3 and 32.8, respectively. The LL decreases could be a consequence of the addition of the additive particles and their lower affinity for water compared to clay ones, in accordance with Subbarao et al. [26]. Soil PL of 22.8 decreased in the combinations with additives to 20.0 for the P2B, to 20.8 for the P2-12, to 21.7 for the DL and to 19.9 for the GGBS. The 15.6 PI of the natural soil decreased to 14.2, 15.3 and 12.9 for the P2B, P2-12 and GGBS combinations respectively, whereas it increased to 16.6 for DL. These plasticity variations were attributed to different physical and chemical processes between the soil and the additives that would overlap each other. Among them are the modification of the soil granulometry by the additive particles' addition, the filling of voids in the soil structure, the soil flocculation or the occurrence of cementitious hydration reactions [26–28].

These effects were also observed in the combinations of the DMRRs with GGBS at different ratios, where the small LL and PL variations produced low plasticity variations.

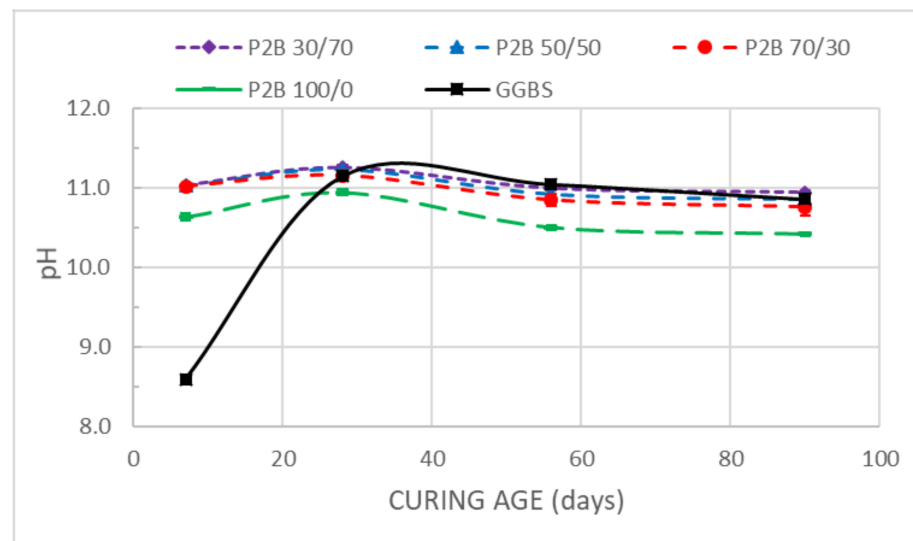
Table 4. Atterberg liquid limit (LL), plastic limit (PL) and Plasticity Index (PI) of the combinations considered in the laboratory investigation.

COMBINATION	LL	PL	PI
SOIL	38.4	22.8	15.6
P2B (100/0)	34.2	20.0	14.2
P2-12 (100/0)	36.1	20.8	15.3
DL (100/0)	38.3	21.7	16.6
GGBS	32.8	19.9	12.9
P2B (30/70)	33.1	20.4	12.7
P2B (50/50)	33.1	19.4	13.7
P2B (70/30)	35.3	19.5	15.8
P2-12 (30/70)	34.1	20.3	13.8
P2-12 (50/50)	35.2	20.7	14.5
P2-12 (70/30)	35.8	20.0	15.8
DL (30/70)	37.2	22.1	15.1
DL (50/50)	38.0	22.0	16.0
DL (70/30)	38.5	23.0	15.5

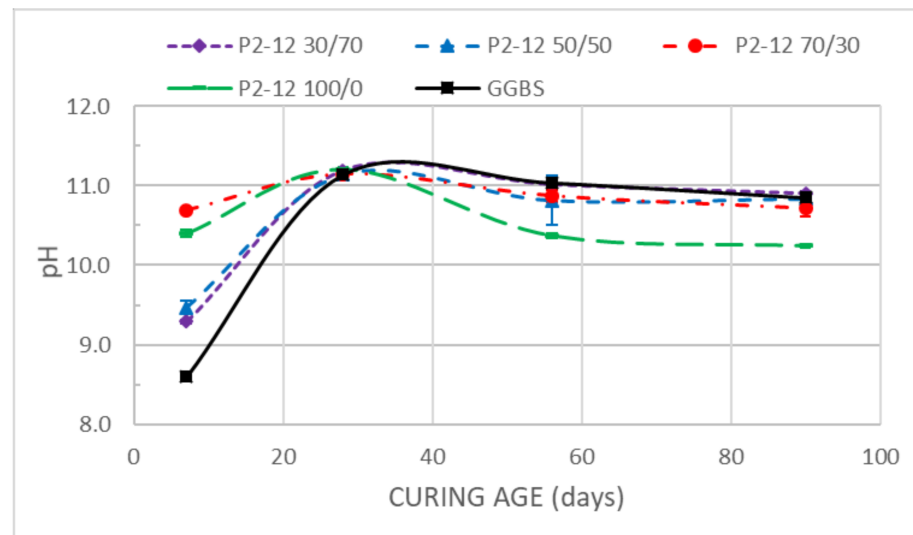
3.2. pH

Figure 2 depicts the evolution of the samples' pH along the 90 days of curing time.

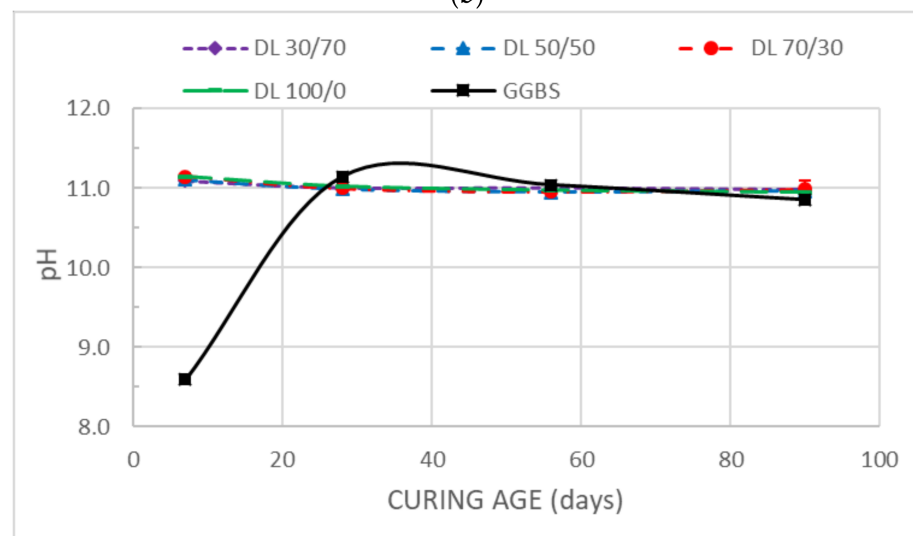
Combinations containing P2B, P2-12 and GGBS showed pH increases from day 7 to day 28. Beyond that point, there was a slight pH decrease up to day 90. On the other hand, DL combinations showed slight pH decreases all along the curing time. These observed behaviors are the consequence of the additive-free CaO and MgO contents as well as of the hydration, dissolution and precipitation mechanisms of the pozzolanic reactions [29,30]. At the earlier curing time, the pH values are explained by the presence of free CaO and MgO in the additives. These oxides hydrate in the presence of water to form portlandite and brucite respectively, that increase the combinations' pH even for low contents of these oxides [31]. This hydration depends on the amount and availability of free CaO and MgO in the additives. In the case of the additives considered in this investigation, for P2B, P2-12 and GGBS, the pH increases were observed between day 7 and day 28. The slowness of the process and the small pH increases demonstrate low availability of free CaO and MgO. For these additives, the highest pH values reached were 11.25, 11.19 and 11.14, respectively. No pH increase was observed for DL, which after 7 days displayed the highest value of the laboratory investigation, with 11.15. This evidenced that this additive contained appreciable contents of available free lime that hydrated before 7 days. These results agree with those of other authors who observed that with high-grade MgO and CaO, the pH increases occurred between 0 and 14 days [30,32,33]. The alkaline environment is required to break the covalent Si-O and Al-O bonds in GGBS and clay particles. There is not a consensus about the pH necessary for this activation process, considering that different authors state that the required pH values are in the range of 11–12 [30]. Afterwards, Ca^{2+} and Mg^{2+} react with Si-O or Al-O to form calcium silicate hydrated (CSH), calcium aluminate hydrated (CAH), magnesium silicate hydrated (MSH) and magnesium aluminate hydrated (MAH) cementitious gels. This process consumes OH^- , producing the pH decrease of the samples observed [29].



(a)



(b)



(c)

Figure 2. Samples' pH variations along the curing time. (a) P2-B combinations, (b) P2-12 combinations and (c) DL combinations.

3.3. Mechanical Strength

Figures 3 and 4 respectively show the results of the UCS testing of the unsoaked and soaked samples.

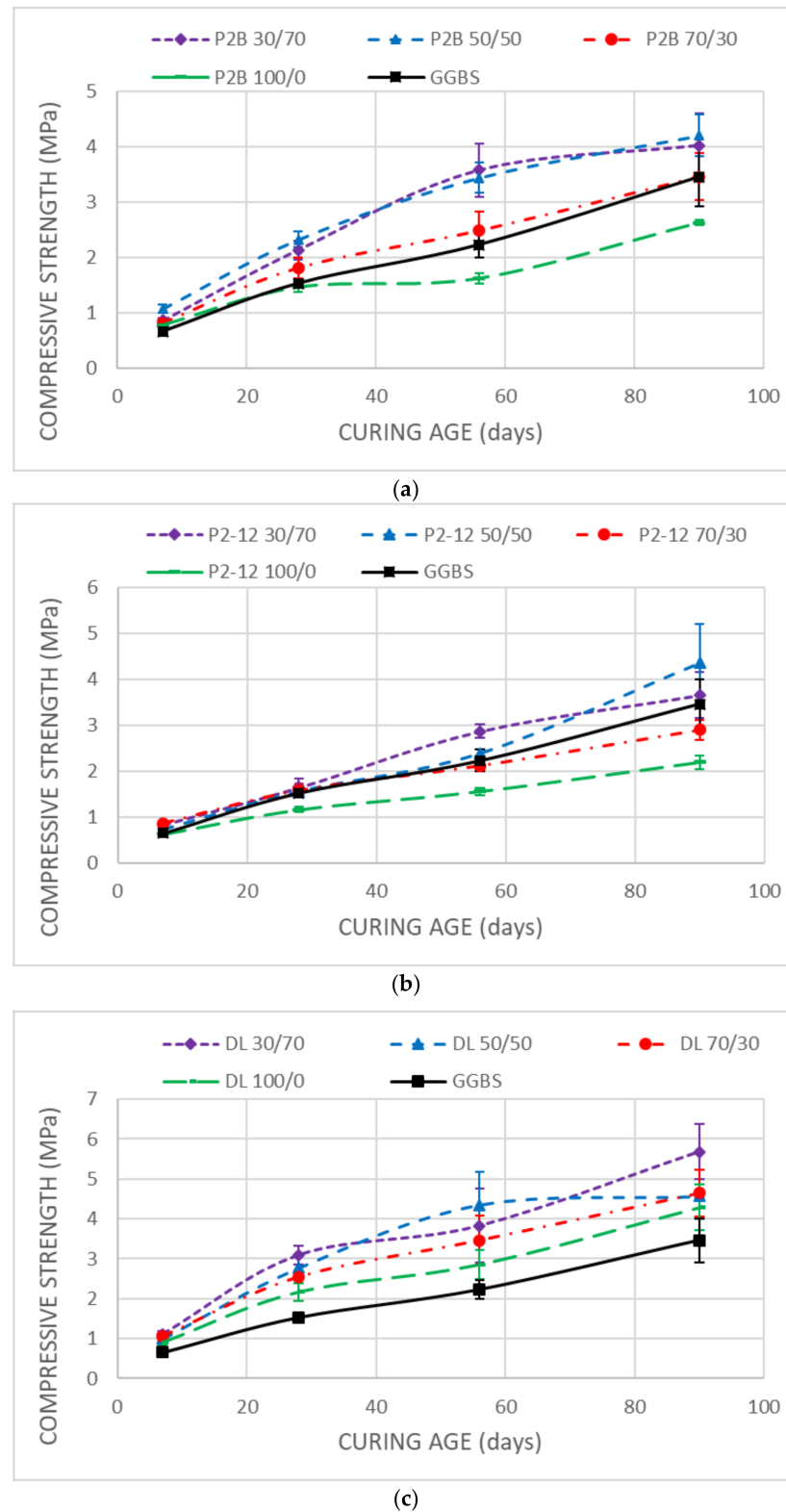
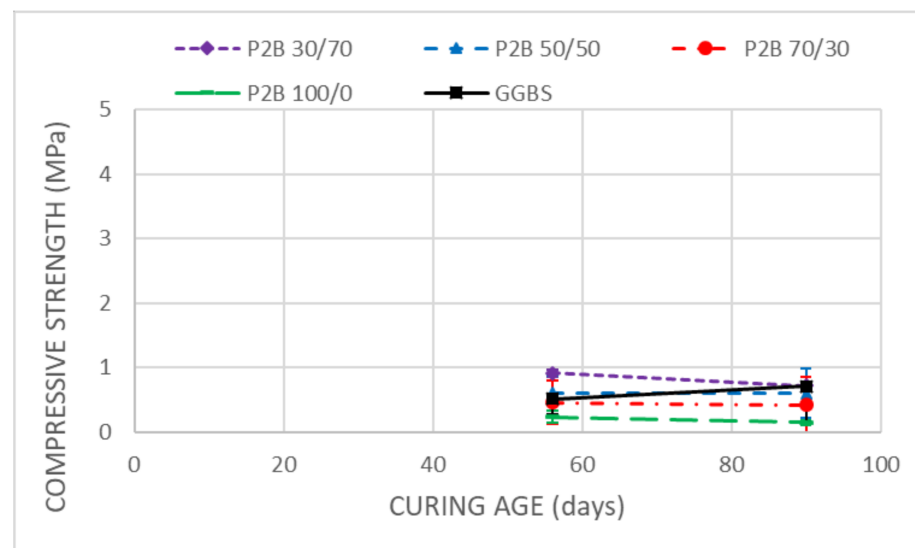
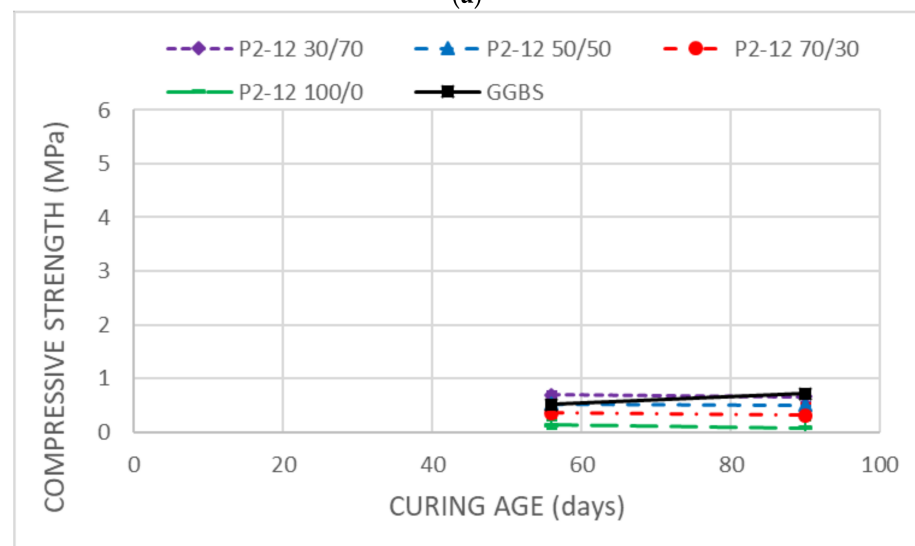


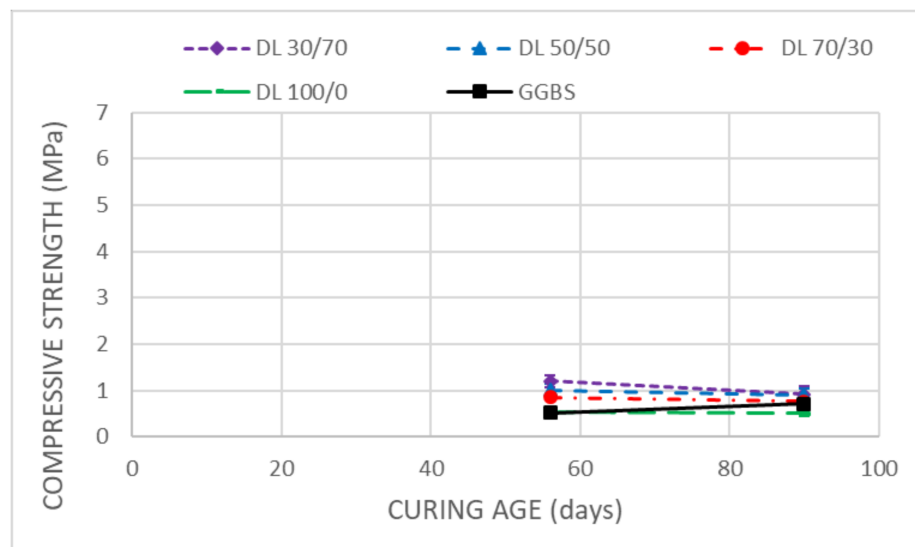
Figure 3. Unconfined compressive strength (UCS) test results before samples' soaking. (a) P2-B combinations, (b) P2-12 combinations and (c) DL combinations.



(a)



(b)



(c)

Figure 4. UCS test results after samples' soaking. (a) P2-B combinations, (b) P2-12 combinations and (c) DL combinations.

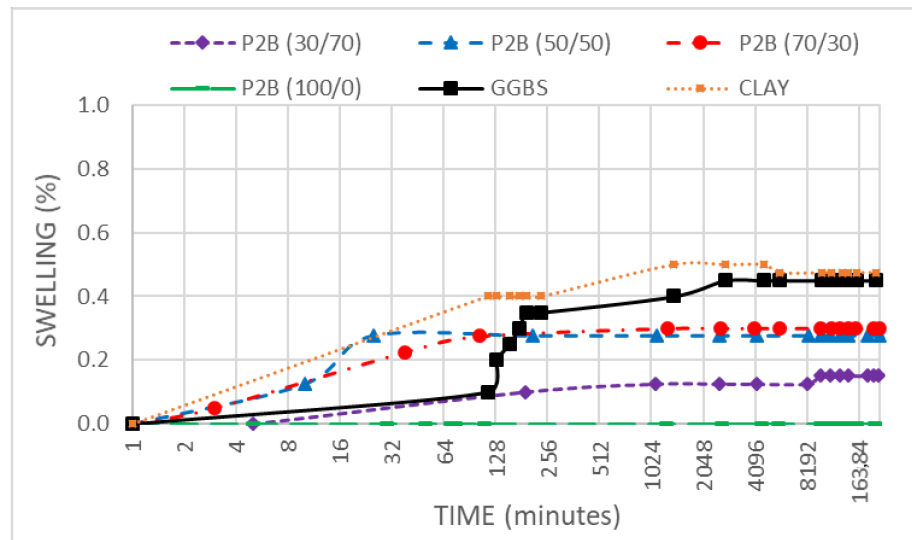
Seven day specimen showed strength results slightly better than the 0.62 MPa achieved by the soil sample. For all the combinations, a direct correlation between the curing time and the combination strengths was observed for the above curing periods. This demonstrated that the additives used had low reactivity that developed over time. When the combinations of the unmixed additives were considered, GGBS showed a better cementitious ability compared to P2B (100/0) and P2-12 (100/0), but lower than DL (100/0), that reached the highest UCS values at all the curing ages. This fact was attributed to the higher richness of reactive CaO in the GGBS, and reactive CaO and MgO in the DL. These oxides from the additives acted as activators of the pozzolanic reactions and combined with their own silicon and aluminum, or with the clay aluminosilicates, to form cementitious compounds. The different amount and reactivity of these oxides present in the additives justify the UCS differences among the unmixed combinations.

Among P2B combinations, P2B (30/70) and P2B (50/50) showed very close UCS results at all the curing ages, overcoming those obtained in P2B (70/30), P2B (100/0) and GGBS combinations. These achieved final UCS values of 4.02, 4.20, 3.46, 2.62 and 3.46 MPa, respectively. This demonstrated the ability of P2B for the activation of the GGBS in the treated soil and the existence of an optimum beneficial effect of the substitution of GGBS by P2B in the range of 30% to 50%. These results agree with the behavior observed between a high-grade MgO and GGBS by Yi et al. [34] and Yi et al. [8]. They found that the optimum content of MgO in the MgO-GGBS binder was close to 20%. The optimum content of P2B in the P2B-GGBS binder obtained in this investigation was between 30% and 50%, highlighting the lower reactivity of P2B compared to a high-grade MgO. P2-12 combinations showed a similar behavior to P2B ones. In this case, all the combinations containing any P2-12-GGBS binders showed close UCS values to those of the GGBS ones at the ages of 7 and 28 days, reaching UCS values in the range of 0.66 to 0.87 MPa and 1.53 to 1.65 MPa, respectively. At 56 days, P2-12 (30/70) had the highest P2-12 UCS result at that stage, with 2.89 MPa. At 90 days, P2-12 (50/50) reached the highest strength among the P2-12 combinations, with 4.36 MPa. This would show a lower reactivity of the P2-12 compared to the P2B, in accordance with its lower effect for the soil plasticity modification. DL (100/0) combination showed improved UCS results compared to GGBS at all the curing ages, demonstrating its higher reactivity and its ability to form cementitious compounds with the soil aluminosilicates. DL (30/70), DL (50/50) and DL (70/30) improved the GGBS and the DL (100/0) UCS results at all the curing ages, evidencing the ability of DL to activate the GGBS. At 90 days, UCS results were 5.68 MPa for the combination DL (30/70), 4.57 MPa for the DL (50/50), 4.64 MPa for the DL (70/30) and 4.28 MPa for the DL (100/0). All of them improved the GGBS result of 3.46 MPa at 90 days. Considering the final UCS results, the optimum DL ratio in a DL-GGBS binder is 30%. This result was the highest UCS of all the combinations considered.

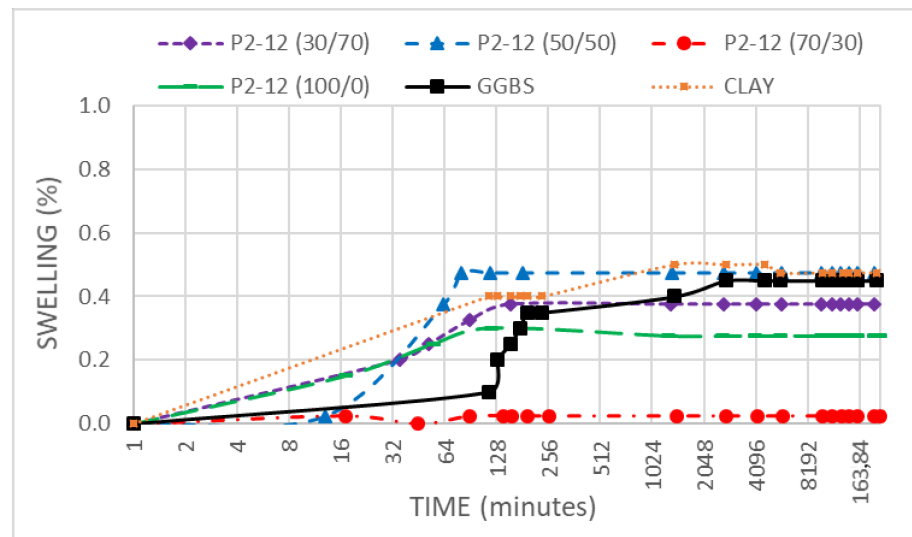
After soaking, UCS results showed strength losses in all the combinations at 56 days as at 90 days, in the range of 68.70% to 94.41%. These losses of strength were attributed mainly to the additive dosages considered in the laboratory investigation and probably to the low UCS results obtained for the unsoaked samples [10]. In spite of the loss of strength, GGBS was the only combination that increased its soaked UCS results at 90 days compared to those at 56 days from 0.04 to 0.05 MPa. On the other hand, the samples containing DMRR reduced their strength after soaking between these curing ages. These results demonstrated that, as expected, water plays a significant role in the loss of strength of the stabilized soils. This behavior is attributed to factors like the change in the soil's pore water pressure, the affinity and the ability to hold water of the cementitious gels, or the soil's plasticity reduction produced by the clay flocculation [35–37].

3.4. Swell Stress

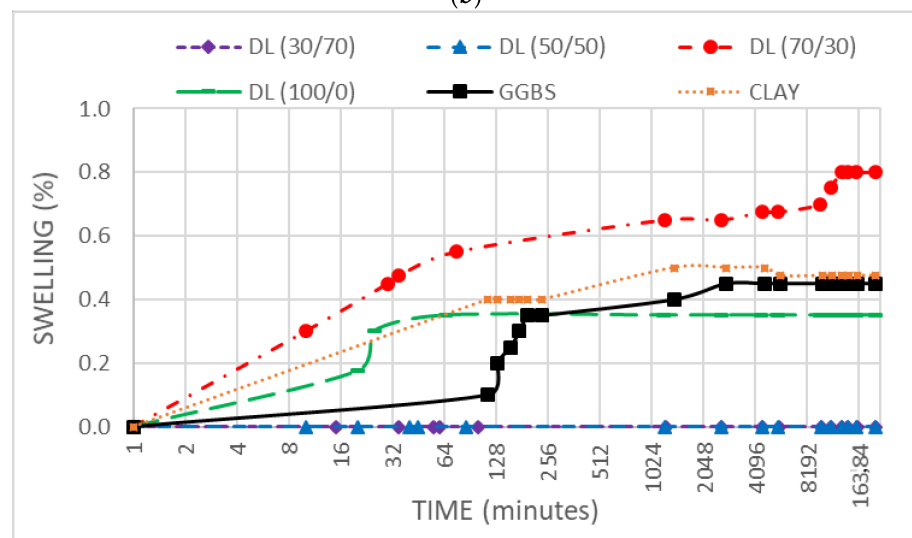
Figure 5 depicts the swell stress results after prolonged exposure to moisture of the soil and the stabilized combinations.



(a)



(b)



(c)

Figure 5. Swell stress test results. (a) P2-B combinations, (b) P2-12 combinations and (c) DL combinations.

The maximum free swelling index of the un-stabilized clay was 0.48%. Three days of testing were required to reach this value. GGBS combination reached a total swelling of 0.45% that stabilized at 2 days of testing. This additive showed a very low effect against the clay swelling that was attributed to its low free lime content. P2B (30/70), P2B (50/50), P2B (70/30) and P2B (100/0) reduced the soil swelling to 0.15%, 0.28%, 0.30% and 0.00%, respectively. These swelling reductions did not show any correlation with the ratio P2B:GGBS of the binder, probably due to experimental uncertainties and the low swell index of the soil and the stabilized combinations. In all of them, the maximum swelling was reached before 3 days of testing, remaining stable afterwards. This demonstrated the nonexistence of possible delayed swelling cases due to the hydration of any P2B constituents. P2-12 (30/70), P2-12 (50/50), P2-12 (70/30) and P2-12 (100/0) combinations reached their final swellings of 0.38%, 0.48%, 0.03% and 0.28% respectively, during the first 3 days of testing. As in the P2B combinations, the swell index obtained in P2-12 combinations did not show any correlation with the ratio P2-12:GGBS. DL (30/70), DL (50/50), DL (70/30) and DL (100/0) combinations respectively obtained final swellings of 0.00%, 0.00%, 0.80% and 0.35%. The general behavior of these combinations was similar to those of the other DMRRs. Among them, only DL (70/30) increased the natural soil's swelling (9 days of testing were required to reach its maximum value). The good results obtained by the combinations DL (30/70) and DL (50/50) were attributed to their close to optimal proportions between the binder constituents. This generated cementitious compounds, preventing any swell. The existence of a delayed hydration processes in binary MgO-GGBS binders was observed by Li et al. [10], but in this case, considering the low swelling values of the DL combinations and the low swelling increase (0.1%) between days 6 and 9, this fact was attributed to experimental uncertainties.

3.5. X-ray Diffraction

XRD tests were carried out in all the treated soil combinations at the ages of 28 and 90 days to identify mineralogy differences among them. The existence of peaks in the stabilized samples that do not appear in the soil diffractogram would be due to the different additive compositions or to chemical changes in the samples because of the cementation process. The intensity of the peaks would be related to the additive dosages or to the formation or destruction of minerals. At the age of 28 days as well as at 90 days, only small differences between the treated samples' mineralogy and the soil were observed. Figure 6 shows the diffractograms of the soil and the P2-12 (30/70) combination at the ages of 28 and 90 days, as an example of the results obtained in these tests.

In all the cases, the crystalline phases of the samples showed the soil mineralogy, which was composed mainly of calcite, quartz, halloysite and albite. The more intense peaks corresponded to calcite and quartz [38]. P2-12 (30/70) samples showed these main peaks, but their intensity decreased slightly due to the presence of the additives that reduced the soil's content in the samples. No minerals from DMRR or GGBS were observed as a result of the low degree of crystallinity of these materials, the low dosage considered and the overlapping of their peak with those of the soil minerals [8,39]. The only hydration product was observed as a peak at 2 theta (35°) that was attributed to the formation of MSH gels based on Reference [38].

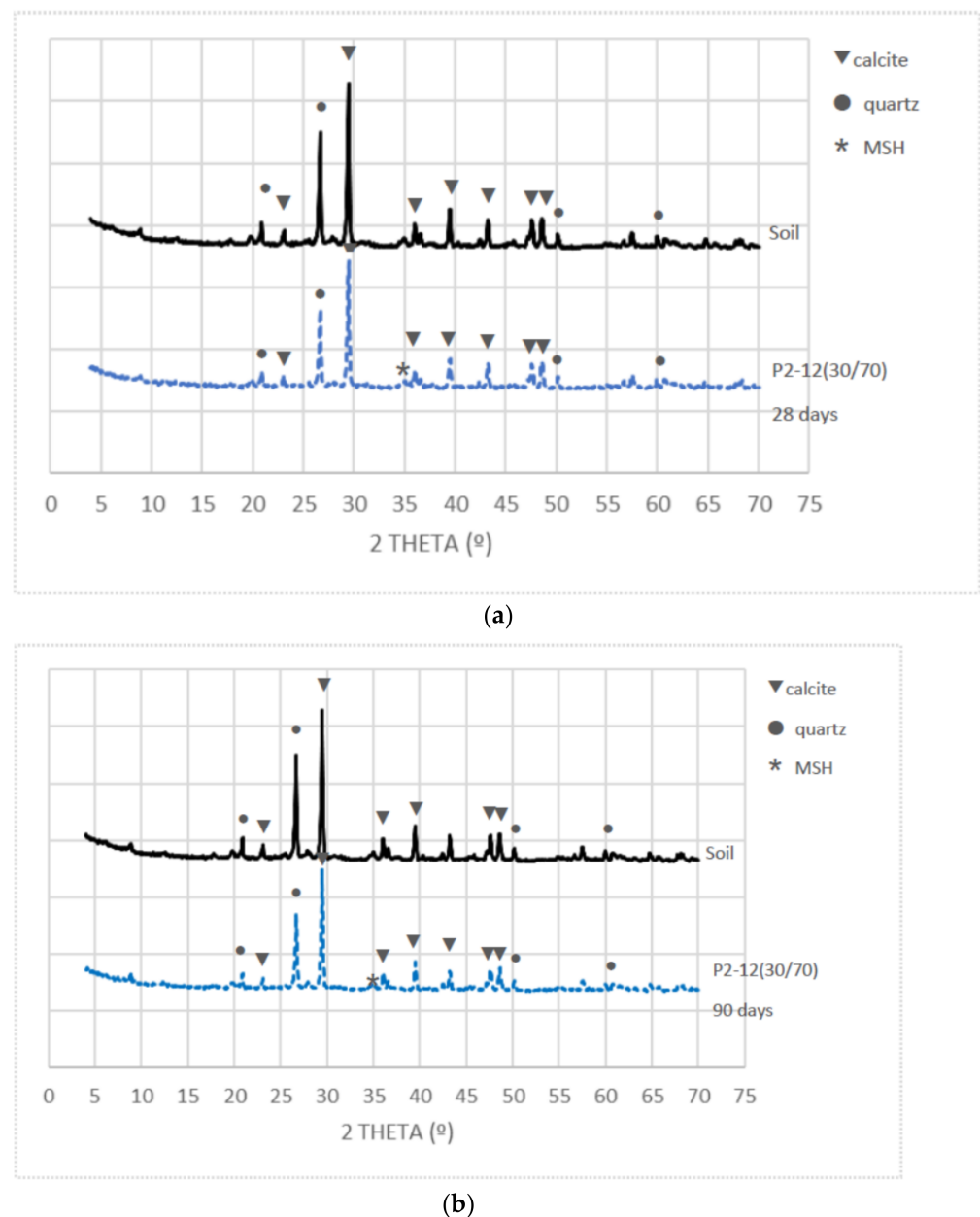


Figure 6. Diffractograms of the soil and the P2-12 (30/70) samples: (a) at the age of 28 days and (b) at the age of 90 days.

4. Conclusions

The goal of this study was to analyze the ability of the DMRR as a source of reactive magnesium for the stabilization of soils, by means of the characterization of physical and chemical properties of samples of clay treated with these products alone and combined with GGBS. Based on the results obtained, the following conclusions were drawn:

1. DMRR and GGBS showed a low effect against the soil's swelling because of their low free CaO and free MgO. The modification of the plasticity observed was attributed to the soil particles' substitution and to a lesser extent to flocculation and cementation processes because of the low reactivity of the additives.
2. The pH values at earlier ages of the stabilized samples are related to the free CaO and MgO provided by DMRR and GGBS, reaching values adequate for the occurrence of pozzolanic reactions. The pH evolution is consistent with hydration and cementation processes.

3. Unsoaked samples increased the UCS results during all the curing time. DMRR demonstrated their ability to stabilize the soil as well as to activate GGBS. The optimum DMRR:GGBS ratio oscillates between 30:70 and 50:50. Based on its chemical composition, DL was the more effective DMRR, as expected.
4. The UCS decreases observed in the stabilized samples after soaking demonstrated that the soil, after the treatment, keeps high affinity and water-holding capacity that diminishes its bearing capacity.
5. The binders considered have demonstrated a low effect against the soil swelling, depending mainly on the DMRR free CaO content. No swelling processes related to delayed MgO hydration were observed.
6. XRD showed that the mineralogy changes in the stabilized samples were mainly due to the particles' soil substitution and the MSH cementitious products' formation.

This work has demonstrated the ability of spent refractory wastes to act as a source of low-grade reactive MgO for the soil stabilization. Although the findings of this investigation are promising, more studies with other refractory materials and other soils are required to increase the knowledge available to date. This way, many of these wastes that so far lack effective valorization methods would become a recycled source of MgO for the manufacturing of low-impact construction binders.

Highlights

1. Spent refractories showed low effect against soil plasticity and swelling
2. Spent refractories show some reactivity due to their pH and free lime and MgO contents
3. Spent refractories stabilized the soil and activated GGBS
4. Stabilized soil keeps high affinity and water-holding capacity
5. No delayed swelling processes related to MgO hydration were observed

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ARTÍCULO 4



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Sulphate soil stabilisation with magnesium binders for road subgrade construction

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ABSTRACT

This paper analyzes the ability of magnesium oxide-based additives to stabilise a low bearing gypsum marly soil, in order to reach subgrade requirements. This soil was not adequate for stabilisation with lime or cement because of its high sulphate content. Binders considered in this investigation were composed of three reactive Mg products and by products, both with and without ground granulated blast furnace slags (GGBS). They were compared to two cements and an aerial lime as soil stabilisers in a laboratory investigation and a field trial. Laboratory tests showed that Mg products with GGBS reached strength results close and at times even better than those of cement. One of the Mg products was the only additive able to reduce the natural soil swelling. Leaching tests demonstrated the ability of the Mg products to reduce the soil leaching of substances like calcium, magnesium, sulphate and chloride. In field trials two of the Mg products combined with GGBS met the bearing capacity requirements for subgrades, in accordance with the Spanish standard.

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Gypsum marly soil; sulphate; soil stabilisation; subgrade; engineering properties

1. Introduction

In geotechnical engineering subgrade is the name associated with the material that supports the road pavement. In-situ soils' strength or stiffness are very often not enough for the subgrade engineering requirements. When that is the case, replacement or stabilisation of the local soil is required to improve the bearing capacity of the pavement foundation (Ward *et al.* 2017, Kakrasul *et al.* 2018, Amini and Ghasemi 2019). Replacing a weak local soil with a better quality one is not always possible because of the unavailability of adequate materials, extra cost or environmental regulations (Ardah *et al.* 2017). Soil chemical stabilisation has been demonstrated to be an effective and economic method for improving the local soil engineering properties (Ceylan *et al.* 2015, Nagrale and Patil 2017, Liu *et al.* 2019). The most common method for soil stabilisation is the addition of cement or lime applied with or without pozzolanic materials like fly ash or ground granulated blast furnace slags (GGBS) (Seco *et al.* 2011a, Puppala 2016, Karatai *et al.* 2017, Ward *et al.* 2017, Ikeagwuani *et al.* 2019, Kakrasul *et al.* 2018, Dheyab *et al.* 2019, Wei *et al.* 2019). Cement and lime get hydrated in presence of water and release OH⁻ ions that increase the pH up to about 12.4. Under these conditions, silicon and aluminium from clay minerals combine with calcium from the additive, generating hydrated cementitious compounds known as pozzolanic gels. These pozzolanic gels are schematically named calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H) and calcium aluminosilicate hydrates (C-S-A-H). These gels are responsible of the enhancement of the engineering properties of the stabilised soil (Nalbantoğlu 2004, Guney *et al.* 2007, Yong and Ouhadi 2007, Chen *et al.* 2009), being responsible for the enhancement of

the engineering properties of the stabilised soil (Nalbantoğlu 2004, Guney *et al.* 2007, Yong and Ouhadi 2007, Chen *et al.* 2009).

Cement and lime manufacturing generate large energy consumption and CO₂ emissions. These considerable environmental impacts have increased last years the interest in more environmentally friendly binders (Phummiphon *et al.* 2018, Amini and Ghasemi 2019, Dheyab *et al.* 2019, Shen *et al.* 2019). However, calcium-based additives are not adequate for the stabilisation of soils containing sulphate (SO₄²⁻). Calcium supplied by lime or cement, as well as aluminium and sulphate from those soils react in the presence of water generating expansive minerals. The most common one is a highly hydrated and expansive crystalline mineral named ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O] (Crammond 2002, Nobst and Stark 2003, Ciliberto *et al.* 2008, Norman *et al.* 2013, Puppala *et al.* 2018). One effective way to reduce the formation of ettringite in a stabilised sulphate soil is the partial substitution of lime or cement by GGBS. GGBS provide a large amount of quickly available alumina and silica, both of which react with the available calcium, expending it for the cementitious gels formation, avoiding the formation of ettringite. GGBS also produce a denser cementitious matrix, reduce permeability and hence water availability, increasing durability against the internal and external sulphate attacks (Tasong *et al.* 1999, Wild *et al.* 1999, Obuzor *et al.* 2011, Seco *et al.* 2017).

Magnesium oxide has demonstrated in MgO-SiO₂-H₂O systems its ability to form nanosized phyllosilicates gels with cementitious properties known as magnesium silicate hydrates (M-S-H) (Li *et al.* 2014, Roosz *et al.* 2015, Bernard *et al.* 2019). MgO can be considered a more environmentally friendly

stabiliser additive than Portland Cement (PC) because of its lower manufacturing impact (Ruan and Unluer 2016). Yi *et al.* (2014) demonstrated that after 28 days the correct proportion of MgO and GGBS overcame the mechanical strength of the soil stabilised with cement. del Valle-Zermeño *et al.* (2015) demonstrated the reactivity and convenience of low-grade magnesium oxides obtained as byproducts in the calcined magnesite manufacturing for environmental applications. Seco *et al.* (2017) observed that a magnesium-based additive enhanced the engineering properties of sulphate soils better than calcium-based ones. In that investigation, five sulphate soils reached unconfined compressive strength above 10 MPa after 21 days, surpassing the requirements of a subbase layer (Ardah *et al.* 2017). Another beneficial effect of the magnesium stabilisation was the decrease of the soils' swell strain after prolonged exposure to moisture. Li *et al.* (2020) demonstrated the advantage of a MgO-GGBS binder in a gypseous soil against swelling and the better strength obtained after samples soaking, compared to cement. These results suggest the potential of stabilisation of local sulphate soils with Mg based binders as road subgrades.

Existing experimental studies of sulphate soils stabilisation are mainly focused on their mechanical strength and engineering properties improvement (Seco *et al.* 2011b, Celik and Nalbantoglu 2013, Mccarthy *et al.* 2014, Seco *et al.* 2017, Behnood 2018). Nowadays there is a lack of knowledge about the effectiveness of the different reactive MgO sources, about the potential releasing of soluble metals and other ions in stabilised soil leaching, and about the load bearing capacity of this kind of stabilised soils. A comprehensive evaluation of the engineering and leaching properties of stabilised sulphate soils with magnesium is crucial. Construction of roads requires a substantial amount of suitable subgrade materials, and leaching could become a threat to the environment. In this study, a sulphate soil was stabilised with a commercial MgO product, two low-grade MgO byproducts generated in the commercial MgO manufacturing process, and GGBS. The use of byproducts containing reactive MgO could become an additional environmental advantage by avoiding the manufacturing of commercial MgO products and by their own valorisation. PC, Sulphate Resistant Portland Cement (SR-PC), and Hydrated Lime (HL) were considered as references. Unconfined compressive strength (UCS), swelling and swell strain after prolonged exposure to moisture, leaching and X-Ray Diffraction (XRD) tests were carried out in laboratory. A field trial was conducted to investigate the load bearing capacity of the stabilised sulphate soil as a road subgrade.

2. Materials and methods

2.1. Materials

2.1.1. Soil

The soil used in this study was a sample of gypsum marl collected in Mañeru (Spain). Marls include a great variety of soft rocks, depending on clay minerals content, cementation process and other geological factors. Environmental conditions such as humidity, temperature, insolation, or freezing-thawing processes, usually modify their physical properties, turning

Table 1. Gypsum marl soil characterisation.

Soil	Gypsum marl
Origin	Mañeru (Spain)
WGS84 coordinates	42° 39' 49.89" N 1° 51' 23.89" W
Atterberg limits:	
LL (UNE 103103)	21.0
PL (UNE 103104)	15.0
PI	6.0
USCS classification	CL-ML
Standard proctor (EN 13286-2)	
Maximum density (g/cm ³)	1.87
Optimum moisture (%)	11.4
CBR index (UNE 103502)	8
Free swelling (UNE 103601)	2.3%
Organic matter (UNE 103204)	0.40%
Soluble sulphates (EN 1744-1)	20.64%
Granulometric curve (EN 933-1)	
Sieve (mm)	% Passing
4	100
1	100
0.63	92
0.40	84
0.25	76
0.08	60.6
Soil mineralogy (X-ray diffraction)	Gypsum Calcite Quartz Dolomite Mica

them into low load-bearing capacity soils. This, in addition to the sulphate content, greatly limits the use of this material in civil engineering. In order to carry out this experiment, one ton of natural gypsum marl was extracted. The sample was homogenised and crushed to a maximum particle size of 1 mm. Table 1 shows the gypsum marly soil characterisation parameters.

Under the Extended Casagrande Classification, this soil belongs to the CL-ML class. The Spanish Road Instruction classify soils from the point of view of their use as building materials, based on their granulometry, Atterberg limits, organic matter content and sulphate content (Ministerio de Fomento 2002). Under this Spanish standard, the sample of soil is classified as 'marginal soil'. This classification limits the use of this material to the foundations and core of embankments and excludes it for the construction of the top of embankments and road subgrades.

2.1.2. Additives

Table 2 shows the richness of the main oxides of interest of the seven additives used in this study.

PC, SR-PC and HL are commercial additives that are usually used as soil stabilisers that were considered as reference. PC and SR-PC were manufactured in accordance with the European Standard EN 197-1 and are respectively marketed under the trade names CEM I 52.5 N and CEM I 52.5 N SR. HL is a commercial hydrated lime CL-90-S manufactured in accordance with the European Standard UNE-EN 459-1.

Three reactive MgO samples were used in the laboratory investigation: a commercial MgO named MCB100 and two byproducts named PC-8 and Sulfamag. All of them are produced in the manufacturing process of the calcined magnesite, as shown in Figure 1.

Table 2. Additives composition and reactivity parameters.

Chemical composition (%)	Ca-based additives			Mg-based additives			
	CEM I 52.5	CEM I 52.5 SR	CL-90-S	MCB 100	PC-8	SULFAMAG	GGBS
SiO ₂	9.17	9.56	0.45	3.41	2.80	1.41	32.18
CaO	76.32	74.43	97.83	3.79	9.10	32.90	43.94
Fe ₂ O ₃	5.63	7.44	0.18	2.90	2.34	1.11	0.33
Al ₂ O ₃	2.96	2.49	0.02	0.82	0.57	0.56	10.40
SO ₃	2.07	2.45	0.43	0.21	6.27	19.71	2.00
MgO	1.08	1.18	0.72	82.26	59.67	25.06	9.05
Loss of ignition at 1050°C	4.97	4.36	25.32	6.61	19.25	19.25	0.91
Citric acid reactivity (minutes)	>600	>600	4	2	29	1119	>600
pH in water (UNE-ISO 10390)	11.88	12.31	12.47	10.88	10.66	12.63	9.82
Free lime (%)	3.67	3.84		1.04	0.81	13.08	0.28

Calcined magnesite is obtained from magnesite rocks. In this case it was calcined at 1050°C to produce a reactive material with low size, high porosity and high specific surface area particles marketed as MCB100. This product is mainly consumed in industry applications that require a high reactive MgO like the gases' desulphurisation. The second MgO source is an MKD recovered from the combustion gases of two kilns, working respectively at 1,100 °C and 1800°C. This dust contains a mix of unburned magnesite, calcined MgO, and occasionally sintered MgO, depending on the part of the combustion chamber where they were pulled from and the higher temperature they were exposed to. This byproduct is marketed under the name PC-8 for the agriculture and livestock industries, wastewater treatment and heavy metals' stabilisation. The third product is Sulfamag. It is a spent hydrated lime used to desulphurise the combustion gases previous to their venting to the atmosphere. Nowadays the most usual application of this product is the fertilisers manufacturing. GGBS is a byproduct obtained during the manufacturing of pig iron. It is formed by rapid cooling of molten iron slag to maintain an amorphous structure and then ground to increase its SSA. As shown in Table 2, it has a large pozzolanic activity potential because of its richness in reactive calcium, silicon and aluminium oxides.

2.2. Samples and field trials manufacturing and testing

Two kinds of samples were prepared during the laboratory investigation. The first category was the samples required to carry out the UCS and leaching tests of the different combinations. The manufacturing process was as follows: soil and additives were mixed in a laboratory mixer for 5 minutes. Water corresponding to the soil Standard Proctor (SP) test was subsequently added slowly. An additional mix was carried

out for 5 minutes to guarantee a complete homogenisation. Once the quality of the mixtures was verified visually, cylindrical samples of 65 mm in diameter and 75 mm high were prepared by pressing the material into a mold, until reaching a 10 MPa pressure at a constant velocity of 50 mm/min. The samples produced were immediately demolded and covered by a polyethylene sheet in order to avoid dehydration. Specimens were cured to the testing age, in a wet chamber at 20 °C and 100% of relative humidity. Table 3 shows the 20 combinations considered for the UCS testing and the constituents' percentages in mass, considering total dosages of 5% and 10%. Once the samples were tested, they were used for leaching and XRD tests.

The combinations with 5% of CEM I, CEM I SR, CL-90-S, PC-8, MCB100 and Sulfamag were picked out to test the swelling, the swell strain after prolonged exposure to moisture of the treated soils because of the formation of expansive gels and their chemical composition. In this case, samples of 50 mm in diameter and 20 mm high were prepared at SP test maximum density and optimum wet content, inside oedometer sample rings. The mixing as well as the sample compaction were performed by hand in accordance with the Spanish standard UNE 103601. Samples were maintained in water immersion and linear expansion was controlled daily by means of dial gauges with an accuracy of 10⁻⁵ m.

The characterisation of the mechanical properties of the laboratory samples was carried out after 7, 14, 28, 56 and 90 days, according to the UCS test defined in the Spanish standard UNE 103400. Previous to the leaching and XRD tests, representative fragments of the specimens tested were crushed and dried for 1 week at 40°C, in a desiccator with silica gel and a CO₂ sorbent, to completely stop the cementation reactions. Leaching tests were conducted on the natural soil, the additives, and the stabilised soil samples on day 28 and day 90, following the procedure

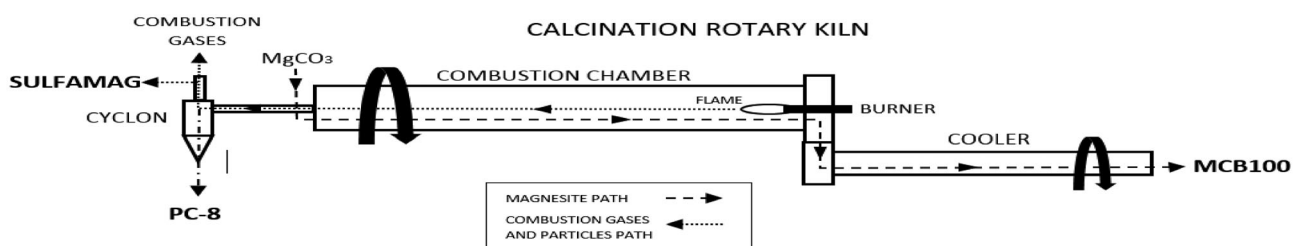
**Figure 1.** Calcined magnesite manufacturing process.

Table 3. Combinations considered for the UCS testing.

Combination	Soil	Ca-based additives			Mg-based additives			GGBS
		CEM I 52.5	CEM I 52.5 SR	CL-90-S	MCB100	PC-8	SULFAMAG	
1	95	5						
2	90	10						
3	95		5					
4	90		10					
5	95			5				
6	90			10				
7	95				5			
8	90				10			
9	95					5		
10	90					10		
11	95						5	
12	90						10	
13	95			1				4
14	90			2				8
15	95					1		4
16	90					2		8
17	95				1			4
18	90				2			8
19	95						1	4
20	90						2	8

Constituents are expressed as dry mass percentage.

defined by the European standard 12457-4. The samples' swelling was tested in the oedometer after 24 hours of testing in accordance with the Spanish standard UNE 103601. The swell strain after prolonged exposure to moisture was analyzed in two ways: On the one hand by the extension of the swelling test to 50 days in order to observe any delayed swelling effect. On the other hand, all the samples at the end of this test were analyzed by XRD to identify any possible mineralogical changes in the samples composition, especially the development of expansive minerals like ettringite or any others able to affect the swell strain after prolonged exposure to moisture of the stabilised soil.

A field trial construction was carried out to test the bearing capacity of the stabilised material. The field trial was constructed in Eugi (Spain), WGS84 coordinates: 43° 00' 33.00"N, 1° 30' 27.04" W. Firstly the in-situ soil was levelled, compacted and the different combination 4 × 5 m reaches were marked by means of stakes. Marly soil was extended and levelled to guarantee a homogeneous layer of 25 cm. On each reach the additives were spread and mixed using a rotavator, making sure not to contaminate the adjacent sections. For this test CEM I, CEM I SR, CL-90-S + GGBS, PC-8+GGBS, MCB100+GGBS and Sulfamag + GGBS combinations at 5% and 10% were considered. Once the different soil and additives mixes were prepared, optimum SP test water content was added by means of a water tank truck and mixed again to guarantee the correct distribution of moisture in the whole sample's thickness. Water content was verified by a nuclear density and moisture gauge. The treated soil was compacted by means of a civil works compactor to the SP maximum density. After 7, 14, 28, 56 and 90 days, according to the UCS, the field trial remained exposed to environmental conditions. Plate loading test, in accordance with the Spanish standard UNE 103808, was performed to evaluate the field soil bearing capacity. This test is currently the only test required by Spanish and international regulations to define the bearing capacity of subgrades. It basically consists of recording the settlements of a steel plate of a known diameter during an initial increasing load cycle,

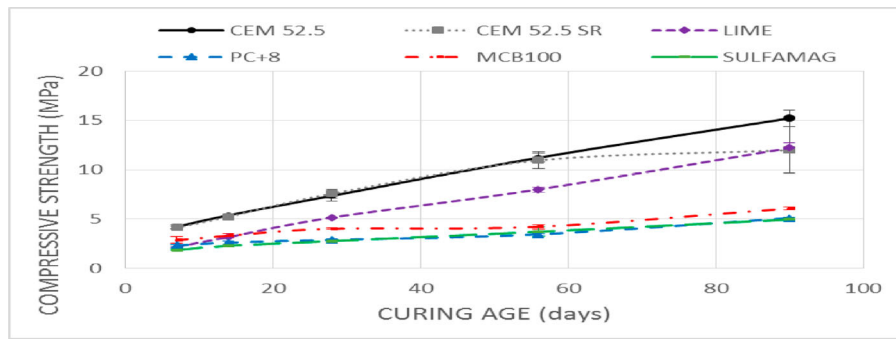
followed by an unloading and a second loading cycle. The result obtained in this test is based on the ratio between the static deformation modulus at the second loading cycle and the static deformation modulus at the first loading cycle (E_{v2}/E_{v1}) (Ministerio de Fomento 2015, Hidalgo-Signes *et al.* 2016). This test was carried out using a plate 300 mm in diameter on day 40 and day 140.

3. Results

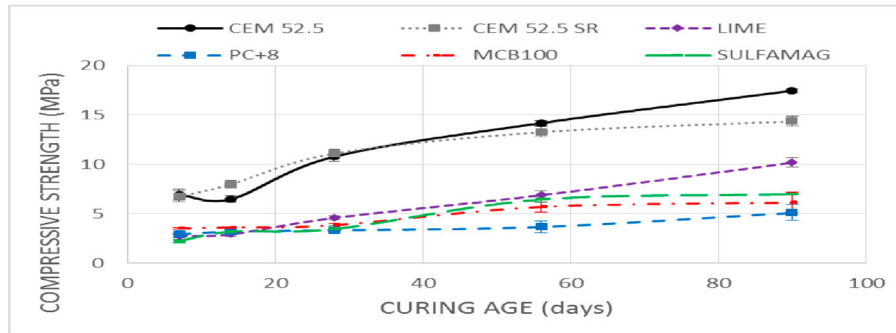
3.1. Unconfined compressive strength

Figure 2(a and b) shows the UCS results obtained by the combinations of soil treated with cements, lime, and the MgO additives.

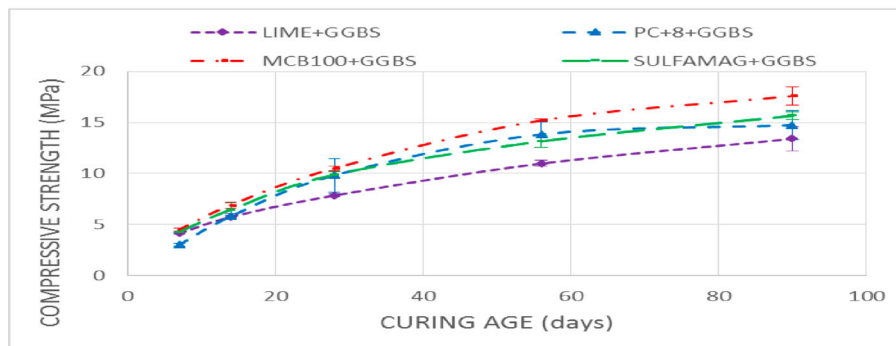
CEM I 52.5 reached the highest UCS for 5% and 10% of dosage after 90 days, with 15.2 and 17.5 MPa, respectively. Because of the reactivity of this cement, the strength of the CEM I 52.5 samples unexpectedly increased for all the curing ages. This could be due to the ability of the $\text{Ca}(\text{OH})_2$ produced as a byproduct of cement hydration to activate the soil aluminium and silicon oxides and generate additional cementitious compounds. After 28 days, CEM I 52.5 SR reached UCS strengths close to those of CEM I 52.5 for a dosage of 5%. Similar results were observed after 56 days for the 10% dosage. At later stages, only small strength increases were observed, showing that this cement had reached its bonding potential in the soil, reaching 12.0 and 14.4 MPa for the dosages of 5% and 10% respectively. It is noticeable that the treatment with 5% of lime achieved a final UCS of 12.2 MPa after 90 days, surpassing the result obtained by CEM I SR. This demonstrates the ability of lime to activate aluminium and silicon from the soil clay matrix to produce cementitious gels. On the other hand, when 10% of lime was used, UCS decreased to 10.2 MPa after 90 days, showing an excess of dosage (Seco *et al.* 2011a). PC-8, MCB100, and Sulfamag showed UCS values in the range of 2–3 MPa for both dosages after 7 days. Samples strength increased slightly over time, with final UCS values



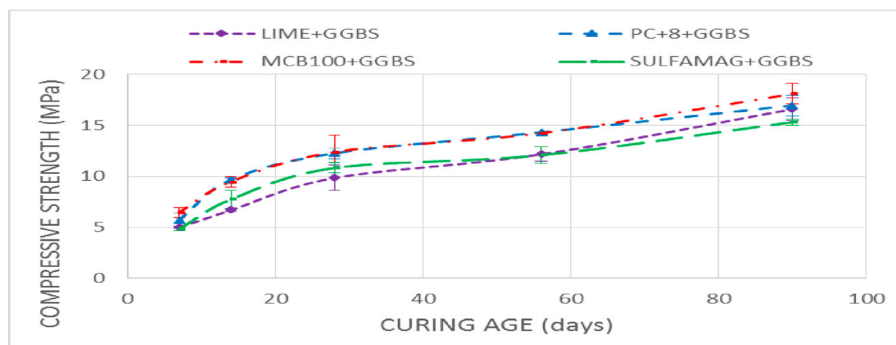
a)



b)



c)



d)

Figure 2. UCS results obtained by the combinations of soil stabilised. (a) cements, lime, and Mg additives at 5%, (b) cements, lime, and Mg additives at 10%, (c) lime and Mg additives with GGBS at 5% and (d) lime and Mg additives with GGBS at 10%.

between 5 and 7 MPa. These results demonstrate that these additives have a lower ability than lime to activate the oxides in a low reactivity soil. This is probably due to the lower content

on reactive MgO and CaO of these products, compared to lime. Sulfamag reached the best UCS among the MgO containing additives with 7.0 MPa after 90 days and 10% of dosage,

highlighting the ability of the CaO as a soil activator. Unexpectedly, but in accordance with the results obtained by Seco *et al.* (2017), no adverse effects related to the presence of ettringite in samples were observed in spite of the high content of sulphate and calcium in many of the combinations.

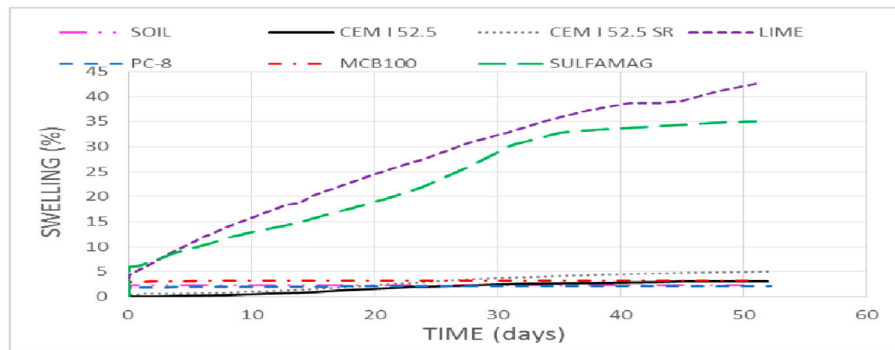
Figure 2(c and d) shows the UCS results obtained when the soil was treated with lime and the MgO additives, combined with GGBS. Samples showed an increase in UCS for all the combinations at all the curing ages and for both dosages, demonstrating the reactivity of the GGBS and the ability of lime, PC-8, MCB100, and Sulfamag to activate it. Apart from day 7 and day 14, MgO additives achieved higher UCS values than lime for the dosage of 5%, demonstrating their ability as activators of the GGBS. Another interesting property observed by using GGBS is the rapid UCS increase at earlier stages because of the GGBS reactivity. GGBS containing combinations, as well as those which did not contain any, showed only small strength improvements when the additive dosages were increased from 5% to 10%. This points out the existence of an optimum additive dosage for an optimum stabilisation of this soil.

The best additive combination containing GGBS was MCB100+GGBS. After 90 days it reached 17.6 and 18.1 MPa for the dosages of 5% and 10%, respectively. PC-8, MCB100, and Sulfamag, combined with GGBS and a dosage of 5%, achieved UCS values that exceeded those obtained by CEM I 52.5 after 90 days. These values demonstrate the advantage of the MgO based additives combined with GGBS for the soil stabilisation.

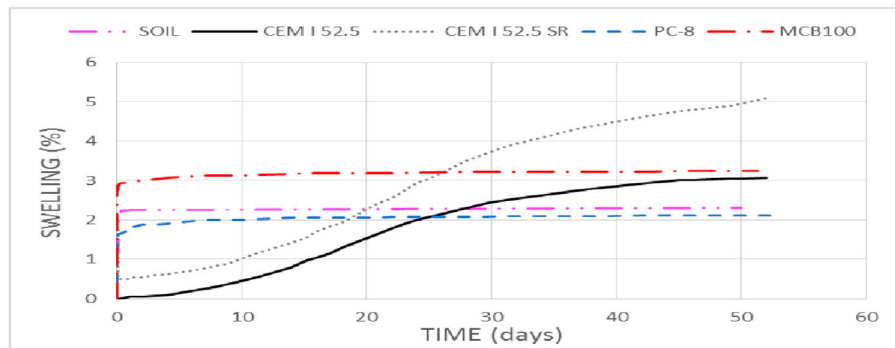
3.2. Swelling and long-term stability

Figure 3(a and b) depicts the soils swell strain after prolonged exposure to moisture after the stabilisation treatment.

After 24 hours, CEM I combination decreased the natural soil swelling from 2.3% to 0.1%, whereas CEM I SR achieved 0.5%. This demonstrates a short-term beneficial effect of these binders on the natural soil swelling. CL-90-S reached 5.3% of swelling, demonstrating the negative effect of the excess of Ca against swelling and the probable formation of expansive compounds. After 24 hours, MCB100 and Sulfamag showed swelling values of 3.0% and 6.2% that were also attributed to the availability of Ca. PC-8 reached a swelling of 1.8% that slightly decreased the natural soil's one. Lime and Sulfamag showed an increasing swelling over the period of 50 days, respectively reaching 42.6% and 35%. This behaviour demonstrates the formation of big amounts of hydrated swelling minerals in these samples, probably ettringite. These swelling values contrast with the lack of damage in the UCS samples and the increasing strength values along the curing time for both combinations. These differences are probably due to the high water availability in the oedometer cell compared to the UCS samples, which favour the ettringite formation. PC-8 sample demonstrated a dimensional stability over time from the beginning and a reduction of the natural soil's swelling. After one day, this combination had reached 1.8% of swelling, and a final value of 2.1% after 50 days. MCB100 sample also showed a swelling of 3% after 24 hours and a swell strain of 3.3% after complete exposure to moisture. These differences between



a)



b)

Figure 3. Swelling and swell strain after prolonged exposure to moisture of the stabilised soil combinations. (a) All combinations swelling and (b) detail of the lower swelling combinations.

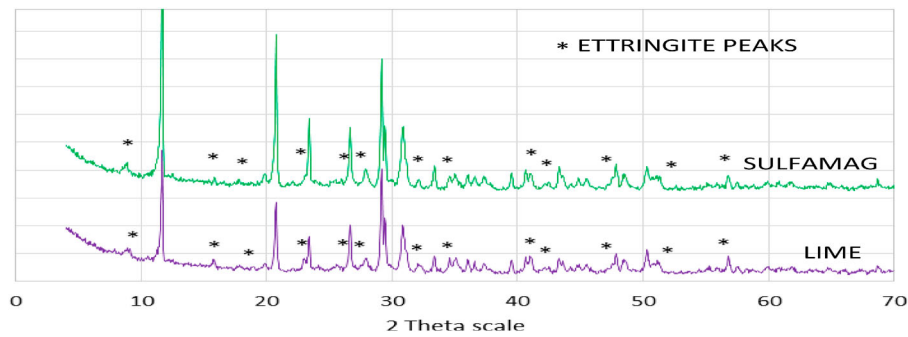


Figure 4. XRD diffractograms of the samples of soil stabilised with CL-90-S and Sulfamag after the prolonged exposure to moisture.

PC-8 and MCB100 could be related to the higher content of free lime in this last product. At the earlier stages, cements showed a decrease of the soil swelling as a result of the presence of CaO. Cement hydration and cementation are quick processes delaying the ettringite swelling, but they do not stop it. Thus, soils with CEM I SR overcame the natural soil's swelling after 20 days and reached a swelling of 5.1% after 50 days. Soils with CEM I overcame the swelling of the natural soil after 27 days and reached a swelling of 3.3% after 50 days. These

unexpected results demonstrated a higher weakness on the ettringite formation of the soil treated with sulfo resistant cement compared to the conventional one.

After observing a macroscopic swelling behaviour of the samples, they were analyzed by XRD to establish the relationship between the observed swelling and the presence of expansive minerals. XRD demonstrated the presence of ettringite in samples of the combinations treated with CL-90-S and Sulfamag. Figure 4 shows how peaks of ettringite appear in the

Table 4. Leaching test results.

Testing method	Unit	Reference	Gypsum marl	CEM I	CEM I SR	PC-8+GGBS	MCB100 +GGBS	Sulfamag + GGBS
(a)								
pH	Electrometry		8.6	11.3	11.5	10.5	10.3	10.9
Conductivity a 20°C	Electrometry		2240	2560	3200	2040	2060	2660
As dissolved	ICP/MS	0.06	0.006	0.03	<0.0025	0.023	0.009	<0.0025
Cd dissolved	ICP/MS	0.02	<0.001	<0.001	<0.0025	<0.001	0.001	<0.0025
Cr dissolved	ICP/MS	0.1	<0.003	0.099	0.10851	0.005	0.009	<0.0025
Pb dissolved	ICP/MS	0.15	<0.002	0.003	<0.0025	0.003	0.004	<0.0025
Ni dissolved	ICP/MS	0.12	0.018	0.014	0.00421	0.011	0.007	<0.0025
Hg	ICP/MS	0.002	<0.001	<0.001	<0.001	0.001	<0.001	<0.001
Ca	Atomic absorption	–	665	533	557	516	504	550
Mg	Ionic chromatography	–	29	0.1	<0.2	0.31	0.42	<0.2
SO ₄	Ionic chromatography	mg/l	1500	1626	1801	1450	1524	1583
Cl ⁻	Ionic chromatography	mg/l	450	13	<3.0	<20	<3.0	<3.0
Total dissolved solids	Gravimetry	mg/l	–	2562	3035	2550	2421	2652
	Testing method	Unit	CEM I	CEM I SR	PC-8 +GGBS	MCB100 +GGBS	Sulfamag + GGBS	
(b)								
pH	Electrometry		11.3	11.4	10.9	11.0	11.1	
Conductivity a 20°C	Electrometry	µS/cm	3370	3380	2620	2790	2750	
As dissolved	ICP/MS	mg/l	<0.1	<0.1	<0.0025	<0.1	<0.0025	
Cd dissolved	ICP/MS	mg/l	<0.1	<0.1	<0.0025	<0.1	<0.0025	
Cr dissolved	ICP/MS	mg/l	<0.1	0.272	<0.0025	<0.1	<0.0025	
Pb dissolved	ICP/MS	mg/l	<0.1	<0.1	<0.0025	<0.1	<0.0025	
Ni dissolved	ICP/MS	mg/l	<0.1	<0.1	<0.0025	<0.1	<0.0025	
Hg	ICP/MS	mg/l	<0.04	<0.4	<0.001	<0.04	<0.001	
Ca	Atomic absorption	mg/l	553	571	536	561	550	
Mg	Ionic chromatography	mg/l	<0.2	<0.2	<0.2	<0.2	<0.2	
SO ₄	Ionic chromatography	mg/l	1550	1560	1370	1490	1410	
Cl ⁻	Ionic chromatography	mg/l	<20	<20	<20	<20	<20	
Total dissolved solids	Gravimetry	mg/l	2840	2880	2410	2590	2380	

(a) 28 days and (b) 90 days.

diffractograms of these samples, revealing the presence of this mineral. These results agree with the swelling behaviour observed in the dimensional stability analysis of the samples, except in the case of the combinations of CEM I and CEM I SR, where the presence of ettringite was expected. This fact, together with the small size of the ettringite's peaks in the diffractograms of the samples where this mineral was observed, suggests, as do Seco *et al.* (2017), that the observed type of ettringite would have a low crystalline structure, or more probably, that it would appear in small amounts, making its identification difficult.

3.3. Leaching

Table 4 shows the leaching parameters, methodology and test results of the natural gypsum marly soil and those of the stabilised soil after 28 days and after 90 days. The column 'reference' shows the limit values for each leaching parameter considered by the Spanish leaching prescriptions to classify a material as 'inert' based on (Ministerio de Medio Ambiente 2013). Shaded in yellow are all the results that exceeded the reference values.

Raw gypsum marly soil overcame the sulphate leaching and it would be classified as 'not dangerous' for the environment. As expected, the combinations of CEM I and CEM I SR increased the soil pH above 11, while binders containing Mg oscillate between 10.3 and 10.9 after 28 days. After 90 days, MCB100+GGBS and Sulfamag + GGBS respectively reached 11.0 and 11.1, because of their content of available CaO hydrating and releasing OH⁻. After 28 days, raw soil as well as the stabilised combinations maintained the leachability of the majority of the metals under the reference values and only

CEM I SR overcame the Cr leaching. An increase in the metals leachability of the combinations stabilised with CEM I, CEM I SR and MCB100+GGBS was observed after 90 days. This increase was attributed to the changes in the cementitious compounds of these combinations over time. The stabilisation had a beneficial effect on the leaching of Ca and Mg. This leachability decreased compared to the natural soil at both curing ages. After 28 days, CEM I increased the sulphate leaching from 1,626 mg/l to 1,801 mg/l, while CEM I SR, PC-8+GGBS, MCB100+GGBS and Sulfamag + GGBS reduced it. After 90 days, all the combinations reduced the sulphate leaching observed after 28 days, reaching PC-8+GGBS, MCB100+GGBS and Sulfamag + GGBS values under the reference to classify these combinations as 'inert'. The stabilisation of this soil reduced the Cl⁻ leaching after 28 days, except for the CEM I SR combination. After 90 days, the Cl⁻ leaching detection limit did not allow to consider if this substance leachability increased but the results in all the cases remained under the reference value.

3.4. Bearing capacity

Figure 5 shows the field trial construction process carried out on 19 May 2019.

Figure 6 shows the meteorological conditions during the outdoor exposition period. At this period, a total rainfall of 284 mm was registered by a meteorological station situated at 2 km from the study area.

Figure 7 shows the field bearing plate testing procedure and Table 5 shows the bearing plate test results of the different combinations of the stabilised soil at the ages of 40 and 140 days.



Figure 5. Field trial construction. (a) gypseous soil layer, (b) binders in big-bags, (c) binders distribution, (d) dry soil-binder mixing, (e) layer watering, (f) wet soil-binder mixing, (g) layer compaction and (h) layer density and moisture control.

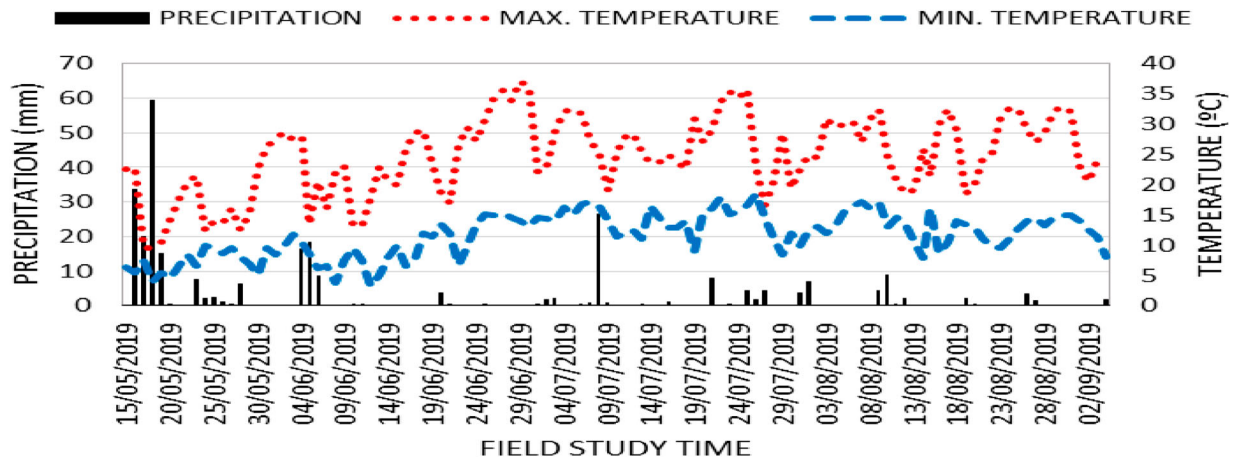


Figure 6. Meteorological conditions during the field study period.



Figure 7. Field bearing plate testing procedure.

After 40 days CEM I, CEM I SR, CL-90-S + GGBS, and Sulfamag + GGBS combinations showed important decreases in the E_{v1} and E_{v2} modulus compared to gypsum marl. This was attributed to the presence of calcium in these additives. The formation of expansive minerals provoked the destruction of the cementitious compounds and the reduction of the bearing capacity of these combinations. CEM I, CEM I SR, and CL-90-S + GGBS also showed important increases of their E_{v2}/E_{v1} ratios that evidenced the low effectiveness of the stabilisation with additives rich in calcium. On the other hand, PC-8 + GGBS and MCB100 + GGBS showed increases of both the E_{v1} and E_{v2} modulus after 40 days, and a decrease of their E_{v2}/E_{v1} ratios down to 1.4 and 1.7 respectively. This highlights the effectiveness of the magnesium-based additives for the soil stabilisation. A noticeable difference of all the combinations' E_{v1} and E_{v2} modulus was observed when comparing day 40 with day 140. This was due to the soil's humidity differences

Table 5. Bearing plate test results of the different combinations of the stabilised soil.

Additive dosage (5%)	40 Days			140 Days		
	E_{v1} (MPa)	E_{v2} (MPa)	E_{v2}/E_{v1}	E_{v1} (MPa)	E_{v2} (MPa)	E_{v2}/E_{v1}
Gypsum marl	46	162	3.5	27	139	5.1
CEM I	8	55	6.9	28	82	2.9
CEM I SR	7	44	6.3	9	116	12.9
CL-90-S + GGBS	7	85	12.1	-	-	-
PC-8 + GGBS	113	156	1.4	34	63	1.9
MCB100 + GGBS	69	117	1.7	57	80	1.4
Sulfamag + GGBS	19	54	2.8	29	65	2.2

caused by the rain between the two testing stages, on 18/06/2019 and 26/09/2019 respectively. Despite this, PC-8 + GGBS and MCB100 + GGBS combinations reached E_{v2}/E_{v1} ratios of 1.9 and 1.4 respectively, lower than the 2.2 required for the stabilised soils in accordance with the Spanish road construction instruction (Ministerio de Fomento 2015).

4. Conclusions

The results obtained in this investigation demonstrated the convenience of the stabilisation of sulphate soils with Mg based binders for road subgrades construction. This general conclusion is based on the following specific conclusions:

- (1) The stabilisation with 5% and 10% of Mg additives improved the mechanical properties of the gypsum marly soil up to usual values obtained with lime in other soils. For both dosages, calcium-based additives reached higher UCS values than Mg ones, demonstrating higher stabiliser efficacy in this soil. Mg additives combined with GGBS reached UCS values close to those of the cements used as references. PC-8 + GGBS and MCB100 + GGBS combinations surpassed the results obtained by CL-90-S combination, demonstrating a higher ability of the Mg additives than lime to activate the GGBS. The minor differences of UCS obtained with the dosages of 5% and 10% pointed out the convenience of the lowest dosage for the stabilisation of this soil. None of the samples showed any damages or lack of strength due to the presence of expansive minerals.
- (2) CEM I, CEM I SR and PC-8 decreased the natural soil swelling after 24 hours while CL-90-S, MCB100, and Sulfamag increased it. In the long term, CL-90-S and Sulfamag showed from the very beginning a high swelling behaviour that was attributed to the ettringite formation. CEM I and CEM I SR also showed a delayed swelling, higher in the case of CEM I SR. These results, in addition to the lack of swelling evidenced in the UCS samples up to 90 days, highlight the complexity of the ettringite formation, which seems to depend largely on the water availability.

- (3) The stabilisation with Mg additives demonstrated their convenience to decrease the soil leaching potential, mainly in the case of sulphate, Ca, Mg and Cl⁻. This allows to classify the stabilised soil in the most restrictive category of the Spanish leaching regulations.
- (4) The field trial demonstrated the bearing capacity of the soil stabilised with PC-8+GGBS and MCB100+GGBS. These combinations reached E_{v2}/E_{v1} ratios adequate for the subgrade construction. The lower bearing capacity of the other combinations was attributed to the formation of ettringite which swelling decreased said combinations' bearing capacity.

The analysis of the results obtained from the different tests demonstrated that PC-8+GGBS was the most effective stabiliser combination. This, in addition to the fact that PC-8 and GGBS are byproducts that allow to valorise low bearing capacity soils as pavement foundations, highlights the environmental convenience of this application.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

The raw data required to reproduce these findings are available from the authors.

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ARTÍCULO 5

Article

Experimental Study of the Valorization of Sulfate Soils for Use as Construction Material

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Abstract: This article shows an experimental investigation carried out for the stabilization of a sulfate soil. The stabilization was carried out in two phases: the first phase was the consumption of the sulfate present in the soil through its controlled transformation into ettringite. After this, a modified soil with lower maximum density, greater optimum moisture identified via standard proctor (SP) test, no plasticity and improved unconfined compressive strength (UCS) was obtained. In the second phase, the modified soil was stabilized by the use of different additives rich in oxides of calcium or magnesium, combined with by-products or waste materials containing reactive aluminum or silicon oxides. As a result, the mechanical strength of the modified soil was improved. In this phase, a binary binder composed of a magnesium oxide product and ground granulated blast-furnace slags (GGBS) obtained the highest UCS. The binary binder composed of lime and an alumina filler formed ettringite in the treated soil. This experiment allowed for the validation of a two-phase stabilization process and the non-conventional additives used, mainly magnesium oxide and GGBS, even for high-bearing-requirement pavement layers' construction.

Keywords: sulfate soil; stabilization; pavement material; civil engineering; ettringite



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1. Introduction

Soil stabilization with chemical additives is a widely used technique in the construction industry. It is particularly suitable for the improvement of the engineering properties of soils containing clay minerals, mainly for the increase in the bearing capacity of fine particle soils, for the construction of pavement layers. This way, the consumption of aggregates in pavement layers' construction decreases, and these low-bearing soils are valorized. The stabilization of a soil also reduces plasticity and swelling, among other usual problems of many clayey soils, favoring the use of these inadequate soils in civil engineering applications such as road construction or urbanization works. Soil stabilization is usually carried out by the use of calcium-based additives such as lime or cement [1]. These additives hydrate in the presence of water, and CaO transforms into Ca(OH)₂. The release of OH⁻ ions in the soil solution produces a pH increase up to 12.4 and clay mineral flocculation due to Ca²⁺ ions' availability. In these conditions, calcium reacts with the silicon and aluminum, supplied by the additive or extracted from the clay matrix, to form cementitious gels that are the responsible of the improvement of the soil properties [2].

Despite the demonstrated suitability of the use of lime and cement as stabilizers for clayey soils, stabilization may cause adverse effects that may even lead to the destruction of the treated soil [3]. One of the most common causes of this type of failure is the presence in the stabilized soil of sulfate (SO₄²⁻). Sulfate is a very common saline component

in many types of natural soils, mainly in the form of gypsum. It can also be present in the water used to compact pavement layers, or can even come from the infiltration of water from the surrounding terrain. The reaction of the Ca^{2+} ions supplied by the additive, aluminum from the clay minerals and the sulfate, with water availability, forms ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$), a highly hydrated and expansive mineral. The adequate conditions for the formation of ettringite are: 1. high pH, 2. availability of reactive aluminum, 3. availability of reactive calcium, 4. presence of sulfate and 5. water availability [4]. Ettringite formation is accelerated by high temperatures (higher than 60–70 °C) [5–8], and with adequate conditions, ettringite can appear even during the mixing of the materials. Ouhadi and Yong [4,9] established the formation of this mineral over one month in one case, and between the mixture of the soil with lime and 48 h in another experiment. Once the ettringite has been formed, the soil is volumetrically stable, and it has been observed that this mineral contributes to improving the soil bearing capacity [5,10,11].

Because of their wide distribution around the world, sulfate soils' stabilization continues to be a necessity, with technical and environmental implications. Sulfate soil stabilization continues being a technical challenge because of the risks associated with the formation of ettringite in the stabilized soil. From an environmental point of view, the stabilization of sulfate soils could contribute to limiting the environmental impact of the construction industry by means of saving natural resources they could substitute. This way, different authors are currently researching this field: Diaz Caselles et al. [12], stabilized a sulfate soil with different hydraulic binders based on calcium. They found that the most effective treatment was obtained with binders rich in GGBS. Although ettringite was observed in this treatment, no volume expansion was observed on the samples. Raja et al. [13] stabilized an expansive soil with a sulfate-resistant cement, rich in GGBS. They found that when the treated soil was exposed to a solution of sulfate, ettringite formed and the soil strength and dry density decreased. Eyo et al. [14] stabilized soils with different sulfate contents using cement and GGBS. They observed the beneficial effect against sulfate attack caused by the substitution of the cement by GGBS. This effect increased as the GGBS content did, mainly for high substitution rates, up to 80%. Other authors have demonstrated the ability of the magnesium-based hydraulic binders for the stabilization of sulfate soils. Seco et al. [3] stabilized five different sulfate soils with lime and a magnesium oxide by-product alone and combined with GGBS. They found that the most effective binder to increase the mechanical strength of the sulfate soils was the mix of GGBS and the magnesium oxide by-product. They also found that the five soils showed increased swelling when they were treated with lime and maintained in water immersion. Four of the five soil samples showed ettringite formation. On the other hand, the soil samples treated with the magnesium oxide showed a decrease in their natural swelling and no expansive minerals were identified on them. Seco et al. [15] studied the ability of a sulfate soil stabilized with cement, sulfate-resistant cement, magnesium oxide by-products and GGBS, to act as a subgrade for pavement construction. They found that cement and a binder composed of magnesium oxide and GGBS were the most effective additives for the improvement of the bearing capacity of the sulfate soil. They also observed unexpected delayed swelling increases when the sulfate soil treated with cement and sulfate-resistant cement was kept in water for more than 20 days.

This work aims to contribute towards knowledge about the now-available technological solutions for the stabilization of soils containing sulfate. For this, a two-phase stabilization method is proposed. The first phase consists of the consumption of the natural sulfate present in the soil through its controlled transformation into ettringite. This way, ettringite would form before the use of the soil as a construction material, becoming a volumetrically stable modified soil with, based on the literature, improved mechanical properties. In the second phase, the treated soil's mechanical properties were improved by the use of additives rich in oxides of calcium or magnesium, combined with by-products or waste materials containing reactive aluminum or silicon oxides. These additives were used like binary hydraulic binders for the development in the treated soil of hydraulic calcium or

magnesium cementitious gels based on [1,3,15–19]. This way, the proposed soil stabilization method would contribute not only to the sulfate soil's valorization, diminishing the risks associated with the delayed formation of the ettringite, but also to the valorization of the recycled additives considered in this investigation. Section 2 introduces the sulfate soil and the additives considered, and shows the sample manufacturing and sample testing methods carried out in the experimental investigation. Section 3 shows the investigation results and the discussion. Section 4 explains the investigation's conclusions.

Highlights

1. A two-phase sulfate soil stabilization treatment was developed;
2. Ettringite formed in a sulfate soil treated with lime and coal bottom ash;
3. The modified soil showed improved engineering properties;
4. Binary binders based on rice husk fly ash and lime or magnesium oxide improved the modified soil mechanical properties;

Lime and alumina filler formed ettringite in the modified soil.

2. Materials and Methods

2.1. Sulfate Soil

The soil used in this experiment is a natural brown tertiary soil, characterized by the presence of levels of clays, sands and silts, with very diffuse laminations marked by color changes and the presence of gypsum. Table 1 shows the soil mineralogy obtained by X-ray diffraction.

Table 1. Sulfate soil mineralogy.

Composition (%)	Compound	Chemical Formula
31	Quartz	SiO ₂
30	Calcite	CaCO ₃
17	Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂
12	Dolomite	CaMg(CO ₃) ₂
10	Chlorite	(Mg,Fe) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈

For the realization of this investigation, one tonne of natural soil was extracted, and after homogenization, the sample was crushed to a maximum particle size of 20 mm. The soil Standard Proctor test (SP) was carried out in accordance with the standard UNE 103501, reaching the sample a maximum density of 1.79 g/cm³ and an optimum moisture content of 14.2%. The liquid and plastic limits tests were carried out in accordance with the standard UNE-EN ISO 17892-12, with a result of 24 and 21, respectively, giving a plasticity index of 3. Soil free swelling was determined by the oedometer test in accordance with UNE 103601, showing no swelling behavior. According to the Modified Casagrande classification system, this soil is of the ML class—sandy silt. The soil sulfate content was estimated at 11%, according to UNE 103201. Based on the Spanish highway construction regulations [20], this sulfate content limits the use of this soil to the construction of cores of embankments with insulation measures to keep the soil away from the entry of water. The soil Unconfined Compressive Strength (UCS) test, according to UNE 103400, returned a result of 0.38 MPa.

2.2. Additives

A commercial CL-90-S hydrated lime was considered as a calcium source for the stabilizing treatments. Different by-products and waste materials rich in oxides of magnesium, silicon and aluminum, suitable for soil stabilization, were also considered. PC-8 is a magnesium-rich kiln dust recovered in the process of the calcined magnesite manufacturing. Rice Husk Fly Ash (RHFA) and Coal Bottom Ash (CBA) are wastes from combustion in industry power plants of rice husk and coal, respectively. Alumina Filler (AF) is generated

during the valorization process of aluminum foundries smelting slag salt. The chemical richness of the considered additives of the main oxides of interest for soil stabilization is shown in Table 2.

Table 2. Chemical composition of the additives considered.

Oxides (%)	Lime	PC-8	RHFA	CBA	AF
CaO	-	8.5	-	38.5	1
MgO	-	72	-	11.4	6
Ca(OH) ₂	97.8	-	-	-	-
SiO ₂	-	3.5	99	36.6	8
Al ₂ O ₃	-	-	-	9.2	70

2.3. Sample Manufacturing

The first step of soil stabilization was the conversion of sulfate into ettringite. Different dosages of lime and CBA were established to guarantee the availability of the oxides required for ettringite formation and the total consumption of the sulfate of the soil. For the manufacturing of each combination, 500 g of soil was mixed with different dosages of lime and CBA for 10 min in a laboratory mixer for sample homogenization. An excess of water for the formation of ettringite was added to the soil. It was estimated as the water required to achieve the optimum moisture content of the SP test plus the water stoichiometrically required for the transformation of the soil sulfate into ettringite. Water was added and the mix was mixed for 10 min to guarantee uniform distribution of the moisture in the sample. After that, samples were placed into closed containers to prevent desiccation and kept at 40 °C until the testing ages of 4, 8, 19, 27 and 52 days. This temperature was chosen to accelerate the formation of ettringite and to prevent the loss of molecular water in the soil minerals. Once we established the most effective additives dosage for the formation of ettringite, a new sample of the optimum combination with 300 Kg of soil was prepared in this way, enough for the rest of the experimental process.

The second stabilization treatment objective was the soil's mechanical strength improvement. To achieve this objective, modified soil was mixed with lime CL-90-S or PC-8, as sources of Ca²⁺ and Mg²⁺ cations, as well as with the other additives rich in oxides of aluminum and/or silicon. Once the samples' homogeneity was guaranteed, the water corresponding to the SP test of each combination were added. Once samples' moisture homogeneity was achieved, cylindrical specimens were manufactured in accordance with the SP test. The curing of each sample was carried out in a closed plastic bag in a humidity chamber at 20 °C and relative humidity of 100% until testing ages of 7, 14 and 28 days.

2.4. Samples Testing

At the considered testing ages, samples of each treated soil combination were conditioned to completely stop the ettringite formation: 50 g of each treated soil combination was ground and added to 250 g of isopropanol in a beaker. The mix was shaken with a glass stirrer for 1 min and then filtered, adding an additional quantity of isopropanol to clean the beaker. Once filtered, the sample was collected and dried for 10 min in an extractor hood, and after that, the sample was maintained for 24 h at 40 °C in a stove. Once the sample was dried, it was maintained in a closed plastic container with silica gel and a CO₂ sorbent until testing. Ettringite was estimated through time by X-Ray diffraction (XRD) using a Power Diffraction File (PDF) of the International Centre for Diffraction Data (ICDD). This test was used to set up the most appropriate dosage of additives, as well as to state the time of ettringite formation [21]. The characterization of the mechanical properties of the stabilized soil samples was carried out according to the UCS test defined in the Spanish standard UNE 103400.

3. Results and Discussion

3.1. Determination of Optimum Dosage of Additives, and Time for Formation of Ettringite

Three dosages of lime + CBA were considered for the consumption of the soil sulfate through ettringite formation: 3%lime + 5%CBA (COMB-1), 5%lime + 5%CBA (COMB-2) and 8%lime + 5%CBA (COMB-3). The evolution of the presence of ettringite in the treated soil samples is shown in Figure 1. Figure 2 shows the XRD diffractograms of the tests carried out in the three combinations considered, at the different curing ages, with the main peaks corresponding to the ettringite marked with an (E).

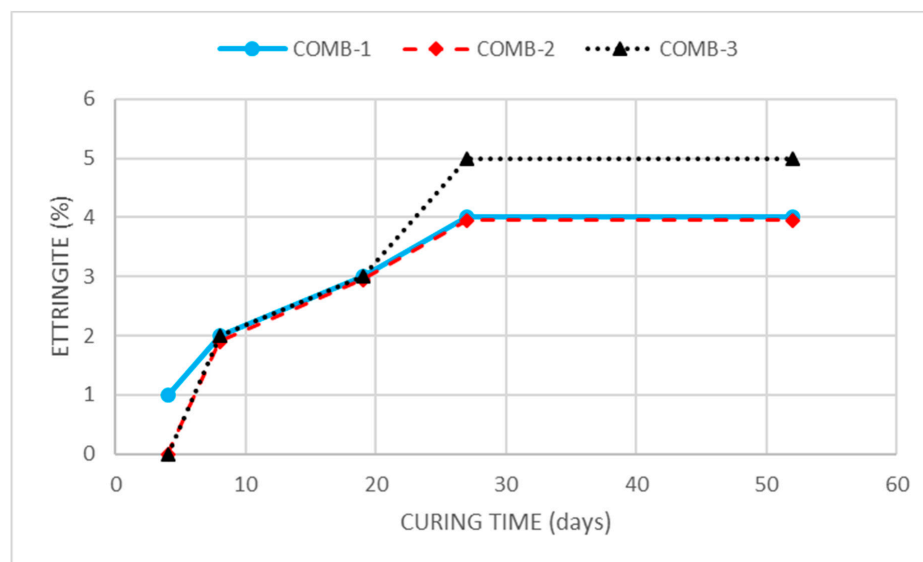
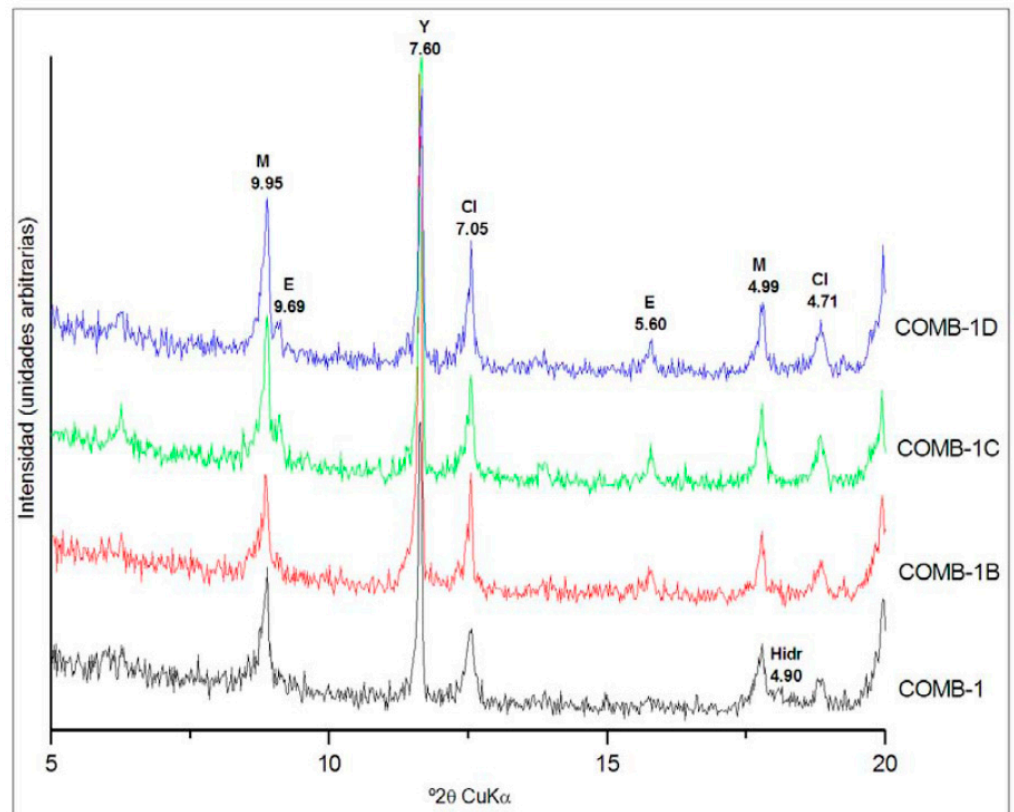
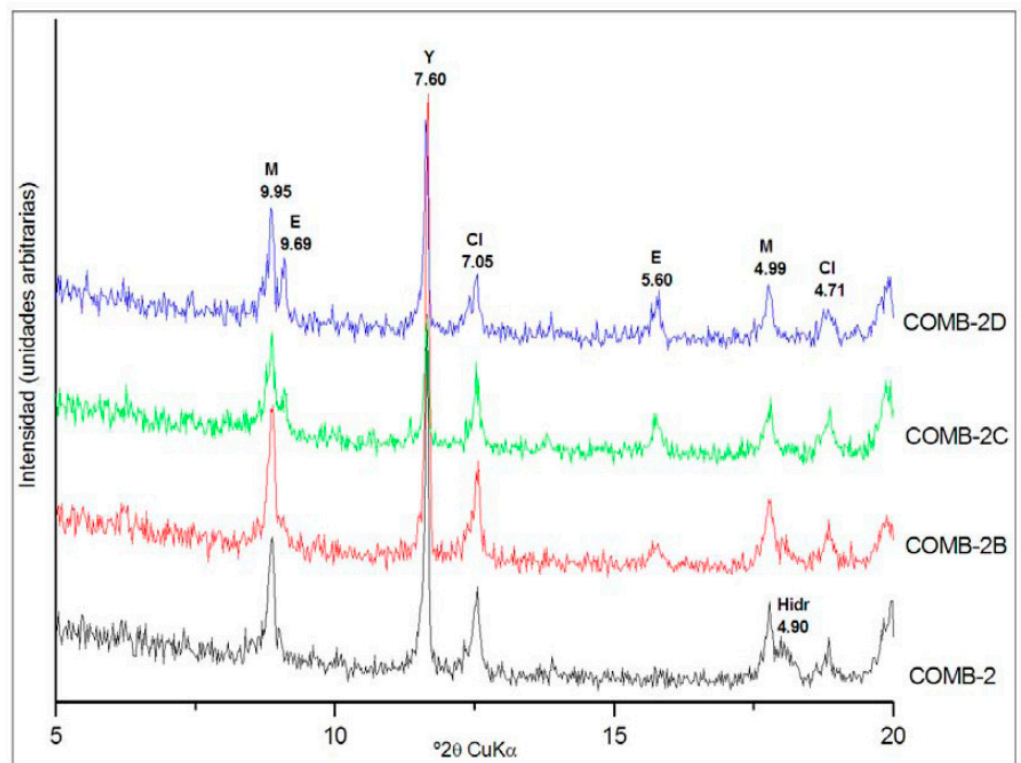


Figure 1. Temporal evolution of the presence of ettringite in the soil samples with different additive contents.

For the three dosages considered, ettringite formed in the soil up to the age of 27 days and then remained stable. The total amount of ettringite produced by the three combinations was very similar, with contents estimated by XRD of between 4 and 5%. Based on these results, the treatment with 5% lime and 5% of CBA was chosen as standpoint of the second part of the stabilization treatment. Despite the fact that combinations 1 and 2 produced the same quantity of ettringite, combination 2 was chosen for the soil modification to prevent the uncertainties in the realization of this treatment and to be sure that all the soil sulfate is consumed. On the other hand, the formation of only 1% more ettringite was not considered sufficient to justify increasing the dosage up to 8% of lime. The curing conditions for the soil modification, 27 days at 40 °C with water saturation, were chosen based on the XRD results, because in the three combinations tested, the formation of ettringite was completed before 27 days. Once the sample of soil required for the second treatment was cured, it was maintained in the stove at 40 °C for 24 h to dry it before its characterization and the realization of the treatment for the improving of its mechanical properties. According to the SP test, the modified soil compared to the natural soil showed a reduction in maximum density from 1.79 g/cm³ to 1.37 kg/cm³ and an increase in optimum moisture content from 14.2% to 30.5%. This reduction in the soil density was attributed to the formation of ettringite and its lower density because of its high degree of hydration. The new optimum humidity was determined by drying the samples at 100 °C, which justifies the increase in humidity obtained, since, in addition to the free water, the water of mineral constitution integrated in the formed ettringite was as well-eliminated. The behavior of the modified soil was non-plastic, and the free swelling in the oedometer test was 0.0%. The compressive strength of the modified soil at 7, 14 and 28 days, reached 0.46, 0.49 and 0.61 MPa, respectively, showing a slight increase compared to the natural soil.

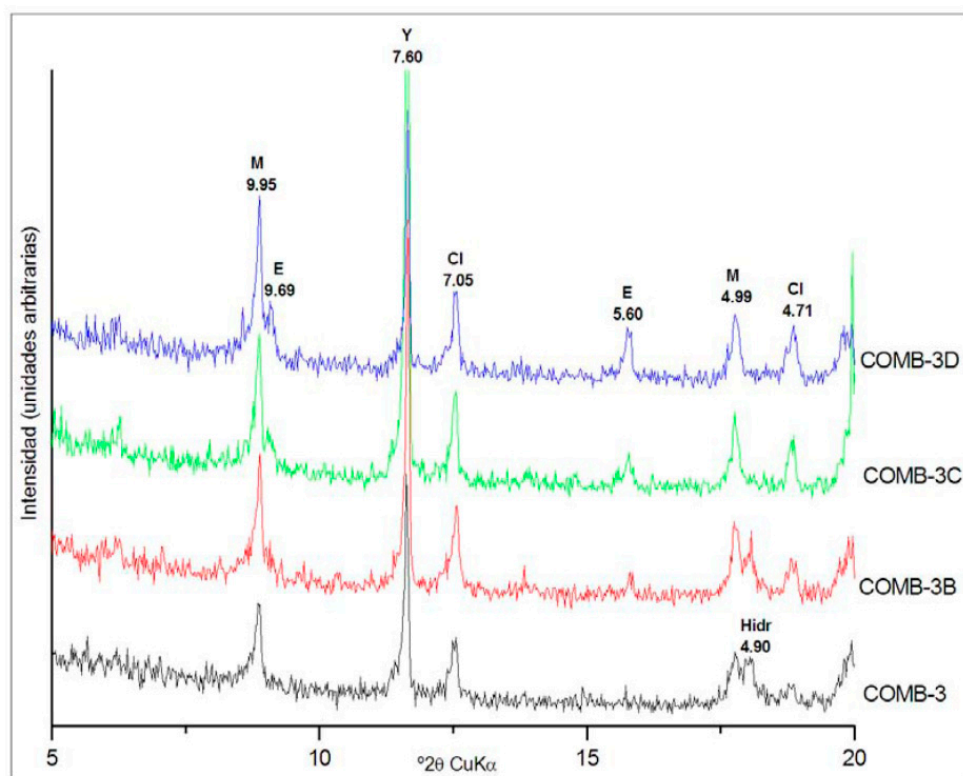


(a)



(b)

Figure 2. Cont.



(c)

Figure 2. XRD diffractograms of the modified soil samples at the curing times of 4, 8 (B), 19 (C) and 27 (D) days. (a) Combination 1, (b) Combination 2 and (c) Combination 3.

3.2. Improvement of Mechanical Properties of the Soil

Once the sulfate was transformed into ettringite, the modified soil received a second treatment in order to increase its mechanical properties. The combinations and dosages of the additives tested are shown in Table 3.

Table 3. Combinations of the modified soil and additives tested for the improvement of the soil mechanical strength.

Combination	Additives
1	MODIFIED SOIL
2	MODIFIED SOIL + 4% LIME + 5% RHFA
3	MODIFIED SOIL + 4% LIME + 5% CBA
4	MODIFIED SOIL + 4% LIME + 5% AF
5	MODIFIED SOIL + 4% PC-8 + 5% RHFA
6	MODIFIED SOIL + 4% PC-8 + 5% CBA
7	MODIFIED SOIL + 4% PC-8 + 5% AF

The maximum density and optimum moisture of each of the combinations was determined according to the SP test, and its compressive strength was determined at 7, 14 and 28 days after the second treatment for the stabilization of the soil. Figure 3 shows the curves of the SP tests of all combinations tested. The use of the additives in this second treatment increased the maximum density obtained and the optimum moisture for all the combinations tested. Combinations 2 and 5 did not change their optimum moisture content compared to the treated soil without additives and reached different maximum

densities. This demonstrates that in these combinations the differences observed depend mainly on the RHFA. With a different behavior, combinations 3, 4, 6 and 7 reached very close maximum density results and showed a reduction in their manufacturing optimum moisture content. This reduction is more evident for the PC-8 than for the lime and for the FA than for the CBA, demonstrating the influence of both binder constituents on the combinations' optimum moisture content.

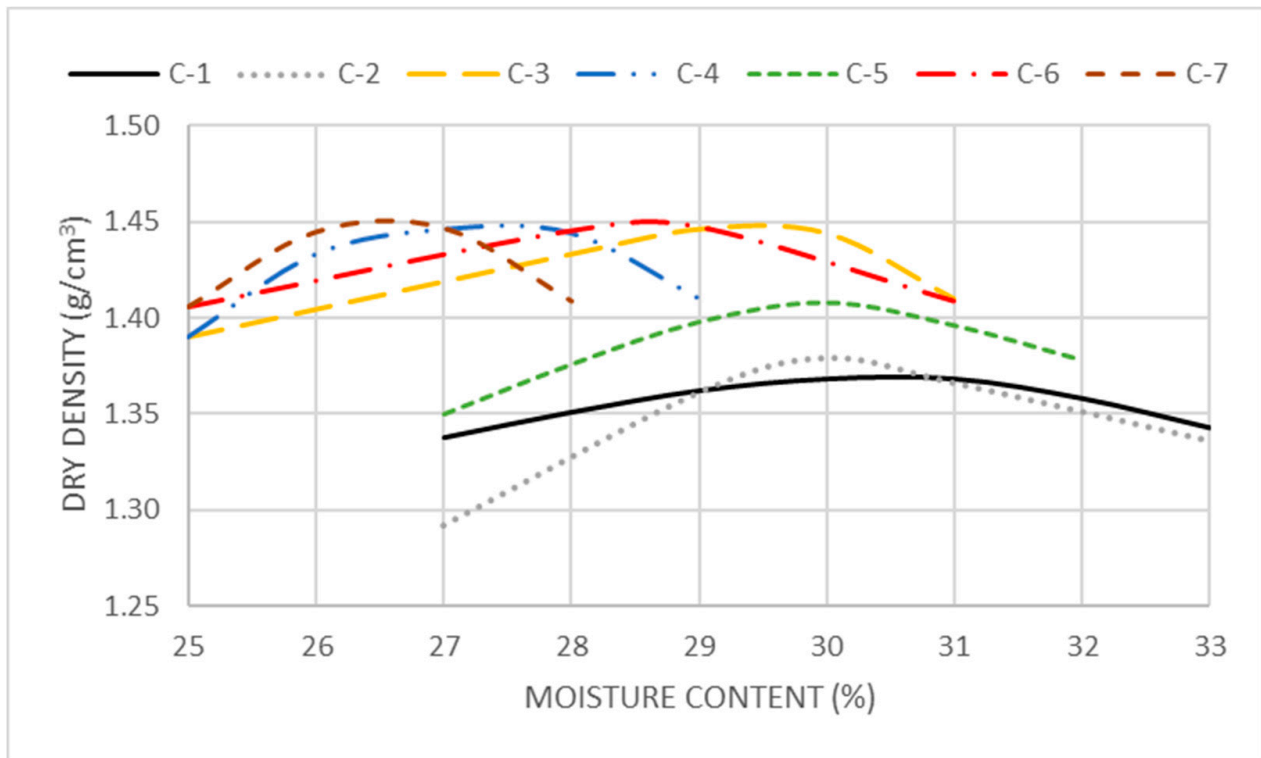


Figure 3. Standard Proctor test curves.

Figure 4 shows the results of unconfined compression tests for each combination at each of the ages considered. The combination formed by the modified soil gave a strength of 0.45 MPa at 7 days, 0.49 MPa at 14 days, and 0.61 MPa at 28 days. This reflects an increase in the unconfined compressive strength of the modified soil compared to the strength of the natural soil. The small increase in resistance observed along the curing time is likely due to the cementitious effect of Ca^{2+} ions not consumed for the formation of ettringite, which generate pozzolanic reactions in the modified soil.

The samples modified treated with lime + RHFA blend (combination 2) and lime + CBA (combination 3) showed unconfined compressive strengths of 0.87 and 0.55 MPa at 7 days, 0.91 and 0.89 MPa at 14 days, and 1.53 and 0.91 MPa at 28 days, respectively. These increases in resistance were attributed to cementitious gel formation in the soil, due to the availability of oxides of calcium, silicon and aluminum. Something similar occurs with the combinations of PC-8 + RHFA blend (combination 5) and PC-8 + CBA blend (combination 6), which reached unconfined compressive strengths of 1.01 and 0.62 MPa at 7 days, 1.69 and 0.74 MPa at 14 days and 2.69 and 0.93 MPa at 28 days, respectively. Combinations PC-8 + RHFA achieved better UCS results than lime + RHFA, demonstrating an improved behavior of the MgO kiln dust compared to lime as an activator of Si and Al sources for the formation of cementitious hydraulic gels, in accordance with Seco et al. [3].

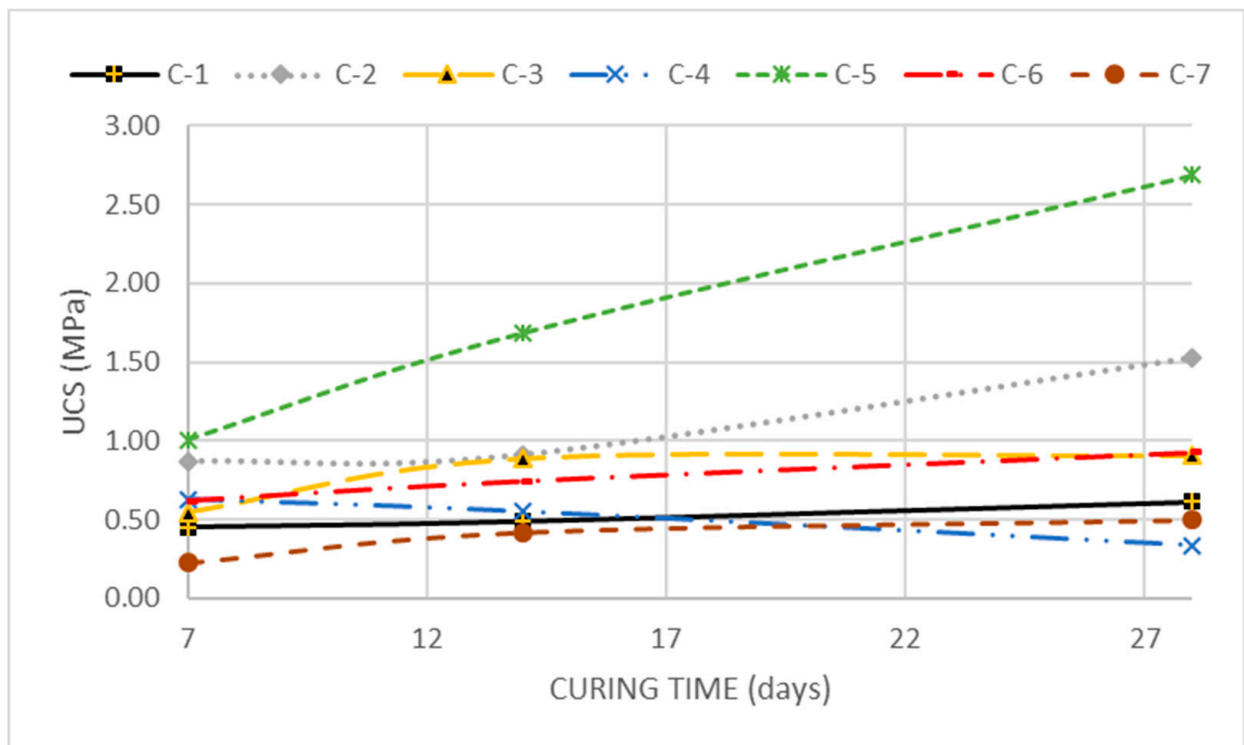


Figure 4. Compressive strength results at 7, 14 and 28 days of curing ages.

Combinations with AF showed anomalous results compared to those obtained with other sources of Si and Al. In the case of combination 4 (lime + AF blend), the values of unconfined compressive strength decreased from 0.63 MPa at 7 days to 0.55 MPa at 14 days and 0.33 MPa at 28 days. Given that aluminum oxide is one of the minerals involved in the formation of ettringite, these anomalously low values of compressive strength have been attributed to the formation of more ettringite, producing a swelling effect in the sample. For combination 7 (PC-8 + AF blend), the compressive strength values reached 0.23 MPa at 7 days, 0.42 MPa at 14 days and 0.50 MPa at 28 days. The increase in the UCS values of this combination demonstrate the effectiveness of the MgO in the formation of cementitious gels, without expansive behavior, even in high-aluminum environments.

Although there are differences between the sulfate soils studied, the binder kinds considered or the binder dosages, the UCS results obtained in this investigation agree with those obtained by other authors. P. Sriram Karthick Raja and T. Thyagaraj [13] reached 3 MPa of UCS at 28 days when they stabilized a sulfate soil with 10% of cement. Eyo et al. [14] obtained up to 1.50 MPa of UCS in soils with sulfate contents in the range 4–12% when they used 9% of cement or a mix of cement and GGBS. On the other hand, the results obtained in this investigation are lower than those obtained by Seco et al. [3], who achieved UCS values above 10 MPa at 28 days for different sulfate soils stabilized with 10% of a binary binder composed of a magnesium oxide by-product and GGBS. These results agree with those of Seco et al. [15], who also reached UCS at 28 days above 10 MPa when they stabilized a sulfate soil with a mix of magnesium oxide and GGBS. These results highlight the convenience of the GGBS as source of silicon and aluminum compared with those used in this investigation, RHFA, CBA and AF. Despite the convenience of the GGBS as stabilizer additive and the fact that it is a by-product of pig iron manufacturing, GGBS is a scarce and expensive product, being nowadays almost entirely consumed by the cement industry. Nevertheless, RHFA, CBA and AF are wastes that in many cases lack effective valorization methods. Indeed, RHFA, the most effective source of reactive silicon considered in this investigation, is available around the world. This way, the use of any waste as a soil stabilizer additive can help to increase the sustainability of the stabilization. On the other hand, combinations 2 and 5 achieve the 1.5 MPa of UCS considered by the

Spanish Road Regulation [20] for the construction of road subgrades, demonstrating the convenience of both combinations for civil engineering applications. As the PC-8 is a by-product, combination 5 is not only the one that achieved the highest UCS results but also a combination in which the binary binder is 100% made of recycled constituents.

4. Conclusions

This experiment showed how a sulfate soil with low mechanical properties can be stabilized for its use as a construction material in civil engineering applications. This valorization process first required sulfate transformation from gypsum to ettringite, and secondly the improvement of the mechanical strength of the modified soil. The formation of ettringite in the considered soil, when the necessary conditions (use of additives rich in the minerals involved in the formation of ettringite, adequate temperature and water availability) were fulfilled, was rapid, with a formation time of less than 1 month in this experiment. As a result of applying this treatment, a soil with modified engineering characteristics was obtained: lower maximum density and greater optimum moisture in SP test, no plasticity and improved UCS. The stabilization of this modified soil with additives (mainly waste materials and industry by-products) rich in oxides of calcium or magnesium, aluminum and silicon, enabled the development of cementitious gels mainly for the combinations treated with PC-8 + RHFA and to a lesser extent for the combination with lime + RHFA. This demonstrated the effectiveness of silicon to form cementitious compounds and the improved ability of magnesium compared to calcium as an activator. This experiment allows for the validation of a two-phase stabilization process and the non-conventional additives used, even for high-bearing-requirement pavement layers' construction. The addition of significant amounts of aluminum caused a significant loss of unconfined compressive strength of the combination containing lime and AF, highlighting the importance of the calcium and aluminum for the formation of ettringite, the most likely source of the loss of resistance and swelling of sulfate soils. Although the results obtained in this investigation are promising, more investigations are required to state the convenience of the proposed stabilization method in other sulfate soils. Depending on the local availability, other additives rich in calcium, magnesium, silicon and aluminum, wastes or by-products preferably, can be tested for sulfate soils' stabilization in other regions for environmental purposes. The use of binary binders based on calcium and aluminum should be avoided because of their potential contribution to the formation of ettringite in sulfate soils.

Author Contributions: A.S.: Conceptualization, methodology, formal analysis, writing—original draft, writing—review and editing, funding acquisition, supervision. J.M.d.C.: Conceptualization, methodology, formal analysis, investigation, writing—original draft, writing—review and editing. C.P.: Methodology, formal analysis, writing—review and editing. S.M.-S.: Methodology, investigation, project administration. E.P.: Methodology, investigation, formal analysis. S.E.: Methodology, investigation, formal analysis. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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9.- INDICIOS DE CALIDAD DE LAS PUBLICACIONES CIENTÍFICAS

Las revistas internacionales en las que han sido publicados los artículos científicos que forman la presente tesis están incluidas en la relación de revistas del *JCR*, como exige el Acuerdo A3/2015 del Comité de Dirección de la Escuela de Doctorado de Navarra adoptado en sesión celebrada el 11 de febrero de 2015 por el que se modifica la normativa para la elaboración de tesis como compendio de publicaciones de la UPNA.

Los indicios de calidad se presentan según los datos más recientes disponibles en la fecha de redacción de la presente memoria, y corresponden a la edición de 2022 del *InCites-Journal Citation Reports (JCR)* de *Clarivate Analytics*.

A continuación, se presentan los indicios de calidad más frecuentemente considerados para analizar la calidad de las revistas científicas:

- **Factor de impacto a 2 años:** Cociente entre el número de veces que han sido citados los artículos de esa revista en los últimos 2 años y el número de artículos publicados en el mismo período.
- **Posición relativa de la revista:** Orden que ocupa la revista con respecto al total de revistas de la misma categoría en el JCR. Las revistas de una categoría se clasifican en orden descendente según el factor de impacto de la misma.

9.1.- INTERNATIONAL JOURNAL OF PAVEMENT ENGINEERING

La revista *International Journal of Pavement Engineering*, con ISSN 1029-8436, es una revista de la editorial *Taylor&Francis*. En la *Figura 37*, se presenta la evolución del factor de impacto de la revista para los últimos 5 años, siendo 4,139 el factor de 2020, año de publicación del artículo.

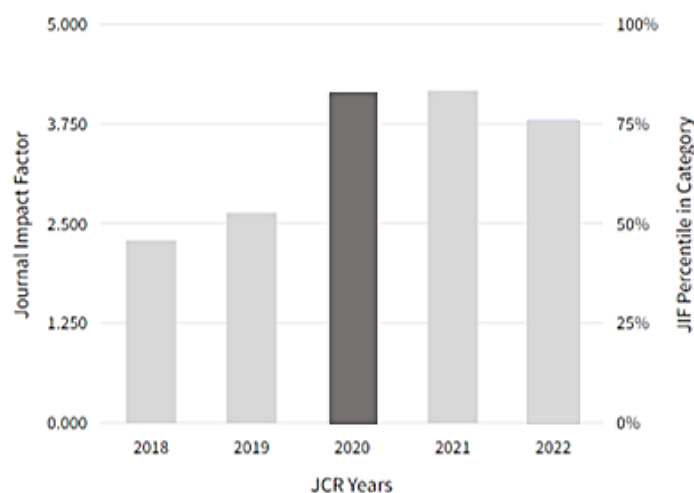


Figura 37. Índice de impacto JCR de la revista. Fuente: <https://www.jcr.clarivate.com/>

La revista *International Journal of Pavement Engineering* en 2020, se encontraba en la posición 16 de las 67 revistas indexadas para la categoría *Construction & Building Technology*, por tanto, es una revista del primer cuartil (Q1). En la siguiente figura se muestra la posición relativa de la revista para la categoría *Construction & Building Technology* en los últimos 5 años.

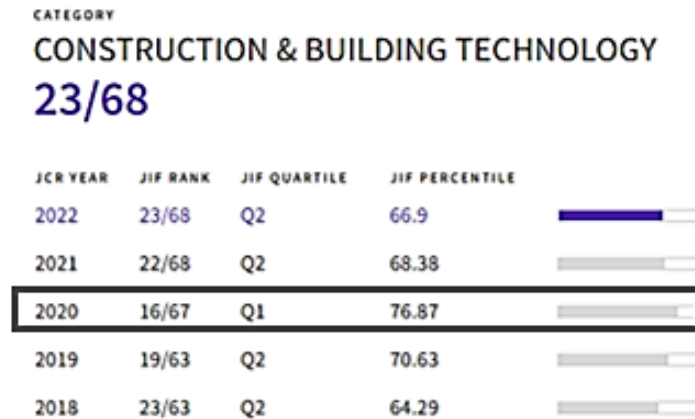


Figura 38. Posición relativa de la revista para la categoría *Construction & Building Technology*.

Fuente: <https://www.jcr.clarivate.com/>

El artículo publicado en la revista *International Journal of Pavement Engineering* y cuyos autores son Andrés Seco, **Jesús María del Castillo**, Sandra Espuelas, Sara Marcelino y Beñat García tiene por título:

"Sulphate soil stabilisation with magnesium binders for road subgrade construction".

Mi contribución personal tanto en la investigación como en la elaboración de la publicación científica fue la siguiente:

- Revisión bibliográfica.
- Desarrollo de la metodología a emplear durante la fase experimental.
 - Fabricación de probetas de suelo estabilizado con los parámetros seleccionados.
 - Realización de ensayos.
 - Diseño y realización de las pruebas de campo.
 - Validación de resultados.
- Análisis formal:
 - Análisis e interpretación de resultados obtenidos.
 - Elaboración de conclusiones.
- Redacción del artículo y elaboración de figuras, tablas y gráficos.
- Revisión y edición final del artículo.

El número de citas obtenidas por el artículo hasta el momento de la redacción de la presente memoria es de 7 según *Scopus*, 13 según *Web of Science*, 22 según *Google Scholar* y 15 según *ResearchGate*.

9.2.- SUSTAINABILITY

La revista *Sustainability*, con ISSN 2071-1050, es una revista de la editorial MDPI. En la *Figura 39*, se presenta la evolución del factor de impacto de la revista para los últimos 5 años, siendo 3,889 y 3,876 el factor de 2021 y 2022 respectivamente, años de publicación de los dos artículos.

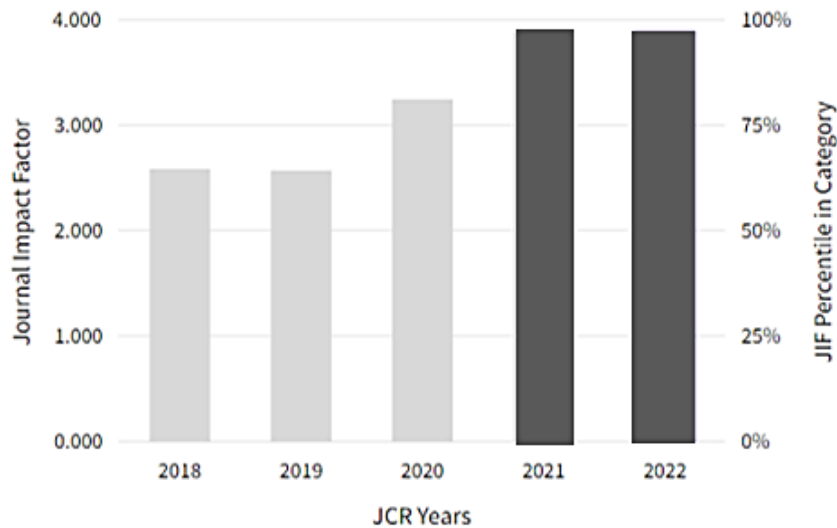


Figura 39. Índices de impacto JCR de la revista. Fuente: <https://www.jcr.clarivate.com/>

La revista *Sustainability* en 2021, se encontraba en la posición 155 de las 325 revistas indexadas para la categoría *Environmental Sciences*, por tanto, es una revista del segundo cuartil (Q2). En el año 2022 se encontraba en la posición 140 de las 330 revistas indexadas para la misma categoría (Q2). En la siguiente figura se muestra la posición relativa de la revista para la categoría *Environmental Sciences* en los últimos 5 años.

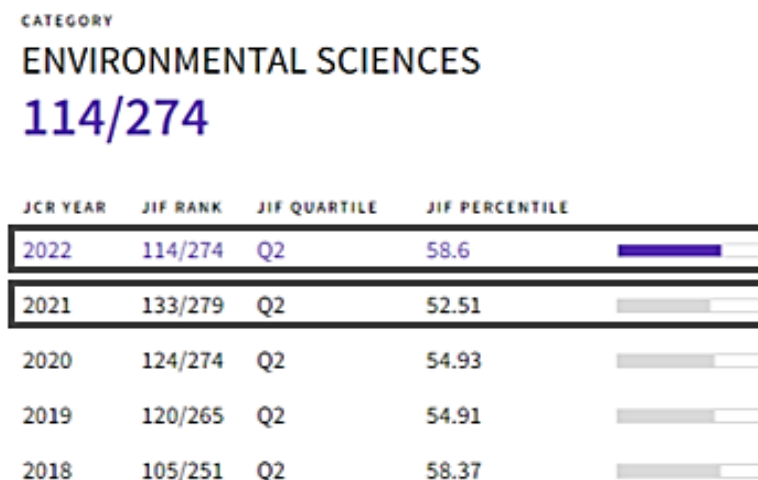


Figura 40. Posición relativa de la revista para la categoría Environmental Science. Fuente: <https://www.jcr.clarivate.com/>

El primer artículo publicado en la revista *Sustainability* y cuyos autores son Andrés Seco, **Jesús María del Castillo**, Sandra Espuelas, Sara Marcelino y Beñat García tiene por título:
"Stabilization of a Clay Soil Using Cementing Material from Spent Refractories and Ground-Granulated Blast Furnace Slag".

Mi contribución personal tanto en la investigación como en la elaboración de la publicación científica fue la siguiente:

- Revisión bibliográfica.
- Desarrollo de la metodología a emplear durante la fase experimental.
 - Formulación de los cementantes alternativos empleados.
 - Fabricación de probetas de suelo estabilizado con los parámetros seleccionados.
 - Realización de ensayos.
 - Validación de resultados.
- Análisis formal:
 - Análisis e interpretación de resultados obtenidos.
 - Elaboración de conclusiones.
- Redacción del artículo y elaboración de figuras, tablas y gráficos.
- Revisión y edición final del artículo.

El número de citas obtenidas por el artículo hasta el momento de la redacción de la presente memoria es de 8 según *Scopus*, 6 según *Web of Science*, 9 según *Google Scholar* y 10 según *ResearchGate*.

El segundo artículo publicado en la revista *Sustainability* y cuyos autores son Andrés Seco, **Jesús María del Castillo**, Celline Perlot, Sara Marcelino, Eduardo Prieto y Sandra Espuelas tiene por título:

"Experimental Study of the Valorization of Sulfate Soils for Use as Construction Material".

Mi contribución personal tanto en la investigación como en la elaboración de la publicación científica fue la siguiente:

- Revisión bibliográfica.
- Desarrollo de la metodología a emplear durante la fase experimental.
 - Formulación de los cementantes alternativos empleados.
 - Fabricación de probetas de suelo estabilizado con los parámetros seleccionados.
 - Realización de ensayos.
 - Validación de resultados.
- Análisis formal:
 - Análisis e interpretación de resultados obtenidos.
 - Elaboración de conclusiones.

- Redacción del artículo y elaboración de figuras, tablas y gráficos.
- Revisión y edición final del artículo.

El número de citas obtenidas por el artículo hasta el momento de la redacción de la presente memoria es de 2 según *Scopus*, 1 cita según *Web of Science*, 2 según *Google Scholar* y 2 según *ResearchGate*.

9.3.- CONSTRUCTION AND BUILDING MATERIALS

La revista *Construction and Building Materials*, con ISSN 0950-0618, es una revista de la editorial *Elsevier*. En la *Figura 41*, se presenta la evolución del factor de impacto de la revista para los últimos 5 años, siendo 7,357 el factor de 2022, año de publicación de los dos artículos.

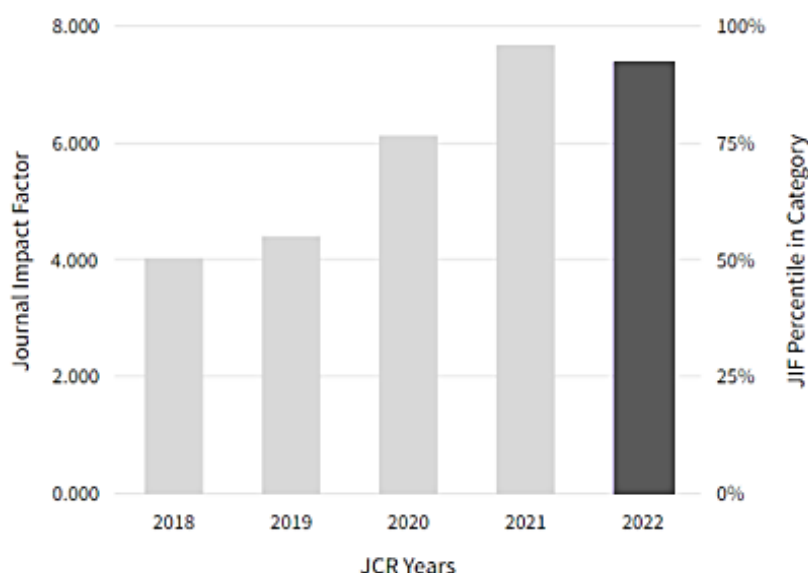


Figura 41. Índices de impacto JCR de la revista. Fuente: <https://www.jcr.clarivate.com/>

La revista *Construction and Building Materials* en 2022, se encontraba en la posición 7 de las 68 revistas indexadas para la categoría *Construction & Building Technology*, por tanto, es una revista del primer cuartil (Q1). En la siguiente figura se muestra la posición relativa de la revista para la categoría *Construction & Building Technology* en los últimos 5 años.

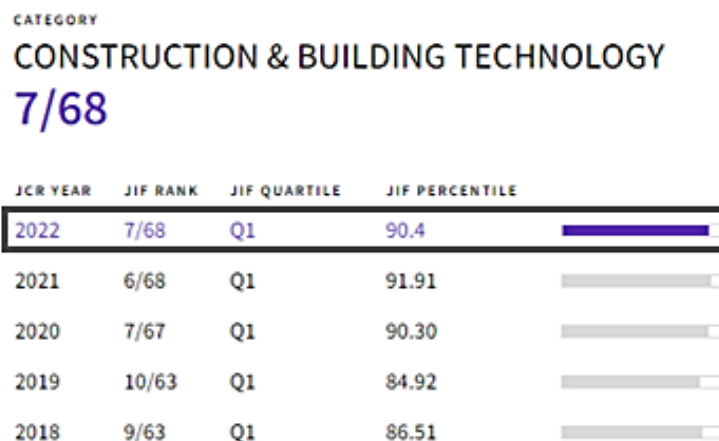


Figura 42. Posición relativa de la revista para la categoría *Construction & Building Technology*.

Fuente: <https://www.jcr.clarivate.com/>

El primer artículo publicado en la revista *Construction and Building Materials* y cuyos autores son Andrés Seco, **Jesús María del Castillo**, Sandra Espuelas, Sara Marcelino y Ángel María Echeverría tiene por título:

"Assessment of the ability of MgO based binary binders for the substitution of Portland cement for mortars manufacturing".

Mi contribución personal tanto en la investigación como en la elaboración de la publicación científica fue la siguiente:

- Revisión bibliográfica.
- Desarrollo de la metodología a emplear durante la fase experimental.
 - Formulación de los cementantes alternativos empleados.
 - Fabricación de morteros con los parámetros seleccionados.
 - Realización de ensayos.
 - Validación de resultados.
- Análisis formal:
 - Análisis e interpretación de resultados obtenidos.
 - Elaboración de conclusiones.
- Redacción del artículo y elaboración de figuras, tablas y gráficos.
- Revisión y edición final del artículo.

El número de citas obtenidas por el artículo hasta el momento de la redacción de la presente memoria es de 1 según *Scopus*, *Web of Science* y *ResearchGate* y 2 según *Google Scholar*.

El segundo artículo publicado en la revista *Construction and Building Materials* y cuyos autores son Andrés Seco, **Jesús María del Castillo**, Celine Perlot, Sara Marcelino y Sandra Espuelas tiene por título:

"Recycled granulates manufacturing from spent refractory wastes and magnesium based binder".

Mi contribución personal tanto en la investigación como en la elaboración de la publicación científica fue la siguiente:

- Revisión bibliográfica.
- Desarrollo de la metodología a emplear durante la fase experimental.
 - Formulación de los cementantes alternativos empleados.
 - Fabricación de gránulos con los parámetros seleccionados.
 - Realización de ensayos.
 - Validación de resultados.
- Análisis formal:
 - Análisis e interpretación de resultados obtenidos.
 - Elaboración de conclusiones.
- Redacción del artículo y elaboración de figuras, tablas y gráficos.
- Revisión y edición final del artículo.

El número de citas obtenidas por el artículo hasta el momento de la redacción de la presente memoria es de 1 según *Scopus*, *Web of Science* y *ResearchGate* y 2 según *Google Scholar*.

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