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Editors

Francisco Agrela Sainz Julia Rosales García Manuel Cabrera Montenegro Carlos Thomas García Fernando López Gayarre

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INTERNATIONAL CÓRDOBA ECO-CONCRETE CONFERENCE

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SCHEDULE

	Il International Córdoba Eco-Concrete Conference	5 july*23
	<u>La Casa del Ciprés</u>	
21:00	RECEPTION CON	FERENCE MEMBERS

	II International Córdoba Eco-	
SESSIONI	Concrete Conference	6 july/23
MUDEJAR ROOM		o july 20
Rectorate of University of Cordoba	Chair. Francisco Agrela	
10.30		RECEPTION
10.00	Inauguration of the Congress by th	e Rector of the University of Cordoba Manuel Torralbo
10:45	WELCO	ME AND INAUGURATION
		JORGE DE BRITO
PLENARY 11:00	Use of s	eawater in recycled aggregate concrete
		UNIVERSITY OF LISBON
	MARIAIS	SABEL SANCHEZ DE ROJAS
PLENARY 11:25	Las puzolanas de	e la antigüedad al futuro: Nuevas investigaciones
		IETcc-CSIC
		TULIO HALLAK
PLENARY 11:50	New trends of	on sustainable sandwich panels
	FEDERAL UN	VERSITY OF SÃO JOÃO DEL-RE
12:15		COFFEBREAK
	(CARMEN ANDRADE
PLENARY 12:45	Recat	ponatación del hormigón
		IETcc-CSIC
	Eco-bormicón:	De la durabilidad al ciclo devida

	II International Córdoba Eco-Concrete Conference La Casa del Ciprés	6 july'23	
20:30	MUSICAL PERFORMAN	ce and gala dinner	



II International Córdoba Eco-Concrete Conference 5-7 July 2023 – Cordoba, Spain

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11:05 a 11:15	Delgado-Plana P., Bueno-Rodríguez S., Eliche-Quesada, D. Use of alternative solid activators waste-based in alkali activated materials from agri-food re	esidues.
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11:55 a 12:05	Gómez-Casero, M. A., Moreno, S., Agrela, F., Cabrera, M., Eliche Quesada, D. Blast furnace slag replaced by biomass bottom ash in the manufacture of Alkali activated of	ements
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12:25 a 12:35	Soriano, L., Borrachero, M.V., Giménez, E., Tashima, M.M., Monzó, J., Payá, J. Influence of accelerators in cement mortars using fluid catalytic cracking catalyst residue (FCC): enhance properties at early-curing ages.	ement in mechanical
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POSTER 3	Cabrera, M., Rancaño, F., Agrela, F., López, M., Rosales, J. Construction of a lorry parking area at the siderurgica sevillana company by reusing steel slag fro	m a landfill site
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EFFECT OF ELECTRIC ARC FURNACE SLAG INTO ECO-CONCRETE

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 LADICIM (Laboratory of Materials Science and Engineering), Universidad de Cantabria. E.T.S. de Ingenieros de Caminos, Canales y Puertos, Av./Los Castros 44, 39005 Santander, Spain

Abstract

Eco-concrete is a robust and stable concrete that uses waste materials as at least one of its constituents or whose manufacturing process does not harm the environment. This study looked into how siderurgical aggregates affected the compressive strength of concrete. The outcomes demonstrate that switching these aggregates out for natural aggregates can improve the strength of the concrete. Concrete's density and compressive strength increase with an increase in replacement rate, reaching a strength increase of up to 31% over control concrete at 100% replacement. The strength of the concrete is also improved by replacing fine aggregate siderurgical aggregates with natural aggregates.

Keywords: eco-concrete, mechanical properties, EAFS, siderurgical aggregates, SA.

1. Introduction

Concrete is the most popular artificial construction material globally due to its adaptability, stability, resistance, and affordable price [1]. In addition, it is highly regarded due to its high mechanical properties, durability, ductility, and fire resistance [2]. Globally, 4.1 billion cubic meters of cement and nearly 10 billion cubic meters of concrete are produced yearly [3]. Sustainable development is the answer to these problems, emphasizing reducing natural and non-renewable energy use, preventing the loss of energy resources, and reducing waste production. Eco-concrete is one strategy for achieving sustainable development [4].

Eco-concrete is concrete made from recycled materials that conserve the environment, uses less energy, and is often affordable [5]. It can reduce building weight, speed up construction, reduce CO_2 emissions by 32%, use 12% more industrial waste products, and require less maintenance and structural reconstruction repair due to behavior similar to compressive strength [6]. Electric arc furnace slag (EAFS) is a hazardous waste that contains heavy metals like zinc, iron, chromium, cadmium [7], and lead [8]. Researchers looked at strategies for stabilizing this hazardous waste due to the large amounts produced, the numerous issues and difficulties associated with its transportation and disposal, and the limited availability of natural resources [9–11]. This study looks at the viability of using steel slag as aggregates in concrete. In addition, this study has looked into the impact of siderurgical aggregates (SA) aggregates from EAFS on the mechanical properties of concrete.



2. Properties of Materials

The components used for samples include cement, sand, aggregates, SA, and superplasticizers. The cement used for this study is Ordinary Portland Cement (OPC) type II with 3000 cm2/g fineness and 3.12 g/cm3 density. For the lubrication of concrete, a superplasticizer based on Ligno. In this research, natural limestone aggregates and SA have been used. The maximum size of aggregate used is 19 mm. Table 1 and Table 2 show the natural aggregates and SA grading analysis results.

Table 1. Chemical properties of materials (%wt.).

Sample	SiO2	Al2O3	Fe2O3	CaO	MgO	SO3	K2O	Na2O	C3A	P2O5	TiO2
Cement	22.00	5.00	3.82	64.00	1.90	1.50	0.49	0.25	6.50	-	1.00
SA	25.80	4.90	31.80	28.60	6.30	-	-	-	-	0.26	0.90

Table 2. Physical properties of aggregates.

Aggregate	Property					
	Apparent Density	Real Density	Water absorption	Porosity	Los Angeles	
	(g/cm3)	(g/cm3)	(wt.%)	(vol.%)	(%)	
Limestone	2.60	2.63	1.35	4.78	22.05	
SA	3.65	3.27	2.5	10.89	18.14	

3. Experimental methods

After determining the mixing plan of control concrete (C) in the first stage, then in the second stage, the natural aggregate of control concrete was replaced with slag aggregate in 25, 50, 75, 100 % in two separate categories of coarse and fine-grains. The mixed proportions used in the present research appear in Table 3.

Codo	Comont	Lime	Limestone (mm)		SA	SA (mm)			G _1
Code Cement		12~19	5~12	0~5	12~19	5~12	0~5	water	sp
С	450	646	315	787	-	-	-	202	0.3
SAC100	450	-	-	787	646	315	-	202	0.3
SAC75	450	161	79	787	484	236	-	202	0.3
SAC50	450	323	157	787	323	157	-	202	0.3
SAC25	450	484	236	787	161	79	-	202	0.3
SAF100	450	646	315	-	-	-	787	202	0.3
SAF75	450	646	315	196	-	-	590	202	0.3
SAF50	450	646	315	393	-	-	393	202	0.3
SAF25	450	646	315	590	-	-	196	202	0.3

Table 3. M	lix design	used for	this study	$(kg/m^3).$
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¹Super plasticizer.



4. Results and Discussion

As shown in Figure 1, samples with coarse aggregates SA represent lower compressive strength than samples with SA fine-grained replacement. However, we observe increased compressive strength by replacing SA aggregates (coarse and fine grain) from zero to 100%. The replacement strengths of 75% and 100% of coarse aggregates are seen to behave similarly and closely, as are 50% and 75% of fine aggregates. The strength of the samples is significantly increased by adding natural aggregates to the top of the consumed aggregates. However, a notable increase in sample density also coincides with this rise in resistance. The strength of 25, 50, and 75% fine aggregate slag samples is equivalent to samples of 25 and 50% coarse aggregates SA after 90 days. The replacement strengths of 75% and 100% of coarse aggregates is significantly and closely, as are 50% and 75% of fine aggregates. However, a notable increase to the top of the consumed aggregates. However, as are 50% and 75% of fine aggregates are seen to behave similarly and closely, as are 50% and 75% of fine aggregates. The strength of the samples is significantly increased by adding natural aggregates. The strength of the samples is significantly increased by adding natural aggregates to the top of the consumed aggregates. However, a notable increase in sample density also coincides with this rise in resistance. The strength of the samples of 25, 50, and 75% of fine aggregates to the top of the consumed aggregates. However, a notable increase in sample density also coincides with this rise in resistance. The strength of samples of 25, 50, and 75% fine aggregates samples of 25 and 50% coarse aggregates sA after 90 days.



- Figure 1. Compressive strength of replaced SA coarse aggregates concrete (up) and SA fine aggregates concrete (down).

5. Conclusions

This study investigated the compressive behavior of SA coarse and fine aggregates in concrete. From the above discussion, the following conclusions can be drawn:



- Adding more than 75% of SA coarse aggregates will not significantly affect the compressive strength of concrete.
- Increasing the amount of SA fine aggregates from 50 to 75% does not increase the compressive strength of concrete.
- The replacement of 100% fine siderurgical aggregate has a more significant effect on the compressive strength of concrete containing this aggregate than the replacement of 100% coarse of this aggregate.
- Adding 25% coarse and fine SA aggregates can obtain good compressive strength compared to samples with only SA coarse or fine aggregates.
- 6. Acknowledgments

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7. References

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RECYCLED FOUNDRY SAND: IMPACTS ON WORKABILITY, MECHANICAL PROPERTIES AND DURABILITY OF MORTARS

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Abstract

The use of by-products from the construction and foundry industry has gained significant attention among researchers and companies aiming to reduce reliance on natural aggregates while promoting waste reduction and a circular economy. This study investigates the workability, mechanical properties, and wear resistance of mortars incorporating varying levels of recycled foundry sand. The results demonstrated that as the recycled foundry sand replacement increased, the workability of mortars decreased, necessitating a higher water/cement ratio to achieve optimal workability. Higher recycled foundry sand replacements also led to decreased flexural and compressive strengths. However, mortars with 25% recycled foundry sand replacement displayed satisfactory mechanical properties comparable to those without recycled foundry sand. Additionally, all mortars met the EN-1338 standard for mechanical durability, exhibiting an abrasion wear mark value below 20 mm.

1. Introduction

Concrete's global usage necessitates continuous quarrying and river exploitation for natural aggregates (NA), leading to shortages and environmental issues from CO₂ emissions during machinery and transportation. To mitigate these concerns, researchers and companies collaborate to utilize recycled aggregates (RA), including siderurgical aggregates (SA) from the steel and foundry sectors, in cement-based materials [1,2]. Recycled foundry sand (RFS), a type of SA obtained from the foundry industry's sand box method, predominantly comprises silica and is influenced by the foundry process and binders used [3]. RFS has been applied in limited amounts (up to 40% replacement) in mortars, concrete, and self-compacting concrete. Several studies report that RFS decreases the workability and mechanical properties of mortars, however, a more extensive study can find the optimal replacement of RFS and w/c ratio to manufacture mortars with similar properties to one made with NA. This work aims to examine the impact of RFS on mortars by varying replacement levels up to 100%, evaluating workability, mechanical properties, and durability. The findings will enhance understanding of RFS applications and promote the development of eco-friendly cement-based materials.



2. Properties of Materials

2.1 Cement and fine aggregates

CEM-I 52.5 R with a Blaine specific surface and density of 4447.2 cm² and 3.05 g/cm³ was used. Silica sand (SS) and RFS with both a density of 2.58 g/cm³ was used. The absorption of the SS and RFS was 0.35 and 3.37% respectively. The aggregates grading curve it is shown in Figure 1.



Figure 1: Aggregates grading curves.

2.2 Mix proportions

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Sixteen mix proportions were made to analyse the influence of RFS in mortars. Cement content was fixed to 500 g, SS content was 1500 g and RFS was replaced by weight. Table 1 shows the mortar mixtures.

	RFS replacement (%)				
	0	25	50	75	100
	0.50	0.50	0.52	0.57	0.67
w/c		0.51	0.55	0.59	0.69
		0.52	0.56	0.60	0.70
			0.57	0.62	
			0.58		

Table 1: Mortar mix proportions.	Table	1:	Mortar	mix	proportions.
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3. Experimental methods

3.1 Workability

The objective of this test was to analyse the influence of the w/c as RFS% increased, based on the workability of the control mortar (0% RFS and 0.50 w/c ratio) by the EN 1015-3 standard.

3.2 Mechanical properties

At 7, 28 and 90 days, the flexural strength of RFS mortar mixes was evaluated following EN-1015-11 using standardized mortar specimens measuring 40 mm \times 40 mm \times 160 mm. Subsequently, the two halves of the mortar were tested for compressive strength using the same standard.

3.3 Wear resistance

At 28 days the mortar specimens were painted in black to observe the abrasion wear marks. Abrasion wear resistance test was performed according to the Annex G of the EN-1338 standard.

4. Results and Discussion

4.1 Workability

Figure 2 shows the influence of RFS and w/c ratio on the slump test. Also, it shows that higher RFS replacement needs an increased w/c ratio for achieving equivalent workability as the control mortar (15 cm). The fitted equations show a consistent linear relationship between increasing w/c ratio and slump for various RFS replacement percentages. The increase of w/c ratio it is because RFS have a higher absorption than the SS and impurities due the foundry process.



Figure 2: Workability of mortars with RFS at different w/c ratios.



4.2 Mechanical properties

Figure 3 shows the results of the mechanical properties of RFS mortars. Figure 2 shows the flexural strength of the RFS mortars. It can be observed that the RFS with 25 and 50% replacement presented an increase in all ages. Regarding compressive strength, Figure 2 shows that at 90 days the RFS mortar with 25% replacement presented a higher resistance than the other mortars. Beyond 25% replacement, the RFS mortars compressive strength decrease at 90 days. This could be due the higher w/c ratios and impurities of the RFS, which affects the bond between the aggregates and the cement matrix.



Figure 3: Mechanical properties of RFS mortars. Flexural strength (left) and compressive strength (right).

4.3 Wear resistance

Figure 4 shows the abrasion wear results of the RFS mortars with the same workability as the control mortar. It is observed that as the RFS replacement increase the abrasion wear mark increase as well, also it is shown that there is a linear correlation between the compressive strength and abrasion wear mark. Being the control mortar the mix with the highest compressive strength and the lower abrasion wear mark. RFS mortars presented higher abrasion wear marks and lower compressive strength, this is because for achieve the same workability as the control mortar, a higher w/c ratio is required, resulting in a more porous material [4].



Figure 4: Abrasion wear mark of RFS mortars (left) and correlation between abrasion wear mark and compressive strength (right).

5. Conclusions

After analysing the results of this work, the following conclusions can be drawn:



- Increasing the RFS replacement reduces the workability of the mixes, making it impractical to manufacture mortars with high RFS replacement and low w/c ratios.
- Low quantities of RFS replacement can lead to a slight improvement in mechanical properties, while high RFS replacement requires high w/c ratios and, consequently, it is not possible to achieve high values of mechanical properties.
- For the same workability, increasing the RFS replacement increases the abrasion wear mark value obtained. Even with a RFS replacement of 100%, the values obtained remain below the most restrictive value, which is 20 mm.

Future studies should be carried out in the field of mortars with RFS to increase the replacement percentage without increasing the w/c ratio, maintaining the same workability.

6. Acknowledgements

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CARACTERIZACIÓN E IDONEIDAD DE LA UTILIZACIÓN DE TRITURADO DE PALAS DE AEROGENERADOR EN LA PRODUCCIÓN DE HORMIGÓN

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Abstract

Muchos de los primeros aerogeneradores están acercándose al final de su vida útil. Así, sus palas deben ser desmanteladas, necesitando soluciones para su reciclaje innovadoras, por los materiales que la componen. Esta solución aborda su tratamiento mediante corte y machaqueo, generando así Triturado de Pala de Aerogenerador (TPA), válido para su incorporación en hormigón. Se realizó un diseño del hormigón específico para contenidos de TPA de hasta el 6% vol., para asegurar su adecuado comportamiento. Además, se desarrolló un proceso de mezcla con 5 etapas con correcciones de plastificante según el porcentaje de residuo añadido. Al añadir TPA al hormigón se obtuvieron mejores resultados en capacidad portante, aunque se produjo una leve disminución en resistencia a compresión. Este enfoque ofrece una solución válida para el reciclaje de palas de aerogeneradores.

1. Introducción

Debido al envejecimiento de los aerogeneradores y desmantelamiento de parques eólicos en los próximos años, el sector eólico debe priorizar el complicado reciclaje de las palas de estos aerogeneradores, haciendo que dicho reciclaje lleve siendo estudiado durante años, pero sin una solución comúnmente aceptada [1].

El tratamiento propuesto aborda el triturado no selectivo de las palas para su incorporación en el hormigón, que produce el residuo denominado por los autores como Triturado Pala de Aerogenerador (TPA). La composición tan variada [2] de estas palas contiene varias fracciones que pueden reemplazar a los áridos naturales y otras que podrían funcionar como fibras recicladas, recuperando y dando utilidad a las palas desmanteladas y mejorando la sostenibilidad del hormigón y su capacidad portante, gracias a las fibras. El objetivo final es definir si esta solución planteada para la recuperación de las palas de aerogeneradores es factible en cuanto al comportamiento (en fresco y endurecido) del propio hormigón, para después avanzar hacia un estudio más detallado del material y su comportamiento en compresión en conjunto con el hormigón.



2. Materias primas sostenibles del hormigón

España se encuentra en la quinta posición mundial en productores de energía eólica y fue pionera en la instalación de aerogeneradores en 1998 [3]. La vida útil de una turbina eólica es de aproximadamente 25 años, por lo que muchos aerogeneradores han de ser desmantelados en los años venideros.

Por lo tanto, el enfoque de este estudio es procesar las palas de los aerogeneradores mediante corte no selectivo y machaqueo, rápido y estandarizable, frente a otros procesos. El residuo obtenido, conocido como Triturado de Pala de Aerogenerador (TPA), es una mezcla integral de los componentes de cada pala, compuesta por fibras de carbono o de vidrio, madera de balsa, plásticos y resinas. Además, las palas incorporan un revestimiento exterior de resina [2] y, en algunos casos, se utilizan rigidizadores de PVC [2], como se puede apreciar en la **Figura 1**.

El proceso consistió en realizar cortes regulares de los paneles sándwich para obtener fragmentos cuadrados de entre 20–30 cm de lado, un primer machacado y tamizado para obtener fragmentos de entre 5–15 mm de tamaño y un segundo machacado y tamizado para tamaño máximo del TPA de 10 mm (**Figura** 1). Todas las características obtenidas se pueden ver en la **Tabla 1**, donde se estudia la idoneidad de este material a la producción de hormigón siguiendo las normas EN-1097-6 y EN 1097-3 [4,5]. La caracterización física del TPA determinó que se puede utilizar en el hormigón como fibras o áridos, debido a la existencia de fibras y microfibras en conjunto con partículas de menor tamaño.

	Densidad saturada con superficie seca (kg/m³)	Densidad aparente (kg/m³)	Composición (% wt.)	Longitud (mm)	Diámetro equivalente (mm)
Conjunto	1630±30	246,64±12,20	-	-	-
Fibras	2040+50 *	-	66,8±3,1	13,07±4,66	0,73±0,14
Poliuretano	2040±30 *	-	8,3±0,3	-	-
Madera de balsa	330±20	-	6,3±0,2	-	-
Microfibras	-	-	13,8±0,5	-	-
Partículas pequeñas no separables	-	-	4,8±0,4	-	-

Tabla 1: Propiedades del TPA

* Densidad medida en ambos componentes, fibras y poliuretano, en conjunto.

3. Método experimental

En primer lugar, se diseñó una mezcla sin contenido de TPA, denominada con la letra R (*Referencia*). Además, se diseñaron dos hormigones diferentes con dos contenidos distintos de TPA: 1,5% en volumen, denominando la mezcla elaborada con este contenido como L (*Low*, "bajo" en inglés) y 6,0% en volumen, denominando a la mezcla correspondiente como H (*High*, "alto" en inglés). Las dosificaciones de las tres mezclas se pueden ver en la **Tabla 2**.





Figura 1: Pala de aerogenerador: Sección genérica con identificación de componentes; Materiales resultantes de la trituración de la pala de aerogenerador (TPA); Componentes separados del TPA.

	Dosi	ficación aju	stada	Dosif	Dosificación para 1 m ³			
DOSIFICACIÓN (kg/ffi ²)	R	L	Н	R	L	Н		
CEM II/A-L 42,5 R	320	320	320	318	312	295		
Agua	128	133	146	127	129	134		
Plastificante 1	2.20	2.62	3.88	2.19	2.56	3.57		
Plastificante 2	1.10	1.31	1.94	1.09	1.28	1.79		
Arena 0/2 mm	500	500	500	497	488	461		
Grava fina 2/6 mm	600	600	600	597	585	553		
Grava gruesa 6/22 mm	900	900	900	895	878	829		
Triturado de Pala de Aerogenerador	0.0	24.5	98.0	0.0	24.0	90.0		
Volumen (litros)	1005	1025	1086	1000	1000	1000		

Tabla 2: Dosificación de las mezclas de los hormigones.

Se adoptó un proceso de mezcla en 5 fases (**Figura 2**), donde se puede observar cómo se separó la mezcla según los áridos, agua, el cemento, los plastificantes y el TPA. Se adaptó el contenido de plastificantes y agua para obtener valores de asentamiento S3 (100-150 mm), habituales en usos estructurales.



Figura 2. Proceso de mezcla en 5 fases.

4. Resultados y discusión

Se realizaron tres probetas cilíndricas de 10 cm de radio y 20 cm de altura de cada una de las mezclas, ensayadas a compresión a 28 días de acuerdo con la norma EN 12390-3 [6].

La mezcla R tuvo una resistencia a compresión de 52,5 MPa, muy parecida a la de la mezcla L (**Figura 3**a). En la mezcla H, se produjo una pérdida de resistencia del 20,4%, que pudo ser producido por una relación agua/cemento más alta (0,45). Se puede observar la pérdida de resistencia a compresión respecto al contenido de TPA en la **Figura 3**b. Respecto a la deformabilidad bajo compresión (**Figura 3**c), se puede ver como la deformabilidad aumentó y, a la vez, la capacidad portante del hormigón. De esta forma, se ve



que las fibras y microfibras consiguieron mantener unida la matriz cementicia incluso tras su rotura, permitiendo así que el hormigón siguiese resistiendo cargas después de su fallo.



Figura 3: Comportamiento del hormigón en estado endurecido: (a) valores de resistencia a compresión, (b) tendencia de evolución de la resistencia a compresión, (c) curvas de tensión - deformación bajo compresión.

5. Conclusiones

Actualmente, hay una necesidad imperiosa de encontrar una solución para el reciclaje de las palas de aerogenerador que llegan al final de su vida útil. Las conclusiones de todo lo expuesto son las siguientes:

- Se requiere de un proceso de mezcla específico, habiendo sido desarrollado en este estudio en 5 fases, para poder asegurar la homogeneidad y la trabajabilidad en fresco necesaria requerida en la práctica habitual para poder añadir el TPA tras el corte no selectivo en el propio hormigón.
- La resistencia a compresión no se vio reducida con contenidos bajos de TPA, pero se vio disminuida en 4,53% por cada 1% de TPA que se añada a la mezcla para contenidos más altos. La deformabilidad y la capacidad portante del hormigón aumentaron, debido al cosido de la matriz cementicia por parte del TPA, produciendo además hormigones más sostenibles.

Por lo tanto, la incorporación del TPA a la mezcla del hormigón es beneficioso para la capacidad portante del mismo, asegurando su trabajabilidad necesaria y la resistencia a compresión requerida. Además, la sostenibilidad asociada al reciclaje de las palas de aerogeneradores resulta aplicable tanto al mundo del hormigón como al sector eólico.

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PRE-INDUSTRIAL SCALE APPLICATION OF STAINLESS STEEL SLAG IN CONCRETE MANUFACTURE

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Abstract

This document studies the substitution of sand and cement by stainless steel slag waste and the subsequent study of the mechanical properties of the slag waste in the application of stainless steel slag waste at the pre-industrial scale in concrete manufacturing. The mechanical behaviour was analysed and very encouraging results were obtained, as this research demonstrates the possible application of stainless steel slag as a construction material in the manufacture of concrete.

1. Introduction

Stainless steel is the fastest growing metal with an annual growth rate of 5.33 % (1980-2019) [1]. Steel production generated a massive amount of slag (≈ 600 MT/year). For environmental and economic reasons, this large volume of slag cannot be deposited in its entirety in landfills, so various treatments and engineering applications are being developed. Depending on the type of steel slag, it can be put to potential use, e.g. electric arc furnace slags (EAFS) have physical properties comparable to natural aggregates, providing high compressive and abrasion resistance. The more basic slags (argon oxygen decarburization units-AODS-, ladle furnaces –LFS-) are potential substitutes as cement binders [2-4].

In general, steel slags have beneficial properties such as good strength, durability and latent pozzolanic (cementitious) properties that make them attractive and potentially suitable for engineering applications, such as infrastructure construction, soil stabilisation, as a filler or binder in concrete [2,5].

The main objective of the research is to study the suitability of Stainless Steel Slag (SSS) for its possible recovery and recycling in the manufacture of conventional HM-20 and HA-25 type concrete, using it as a substitute for sand and/or cement. The mechanical behaviour of specimens manufactured in situ and samples at different ages will be evaluated and suitable dosages will be obtained, which will allow the application of SSS in slabs that will be executed on a real scale.



2. Pre-design of experimental slabs

After characterising the different physical-chemical properties of SSS and testing different dosages in concrete to evaluate its mechanical behaviour, it was decided to carry out the execution of 4 slabs of 2x2 m with a thickness of 15 cm with a mesh at the bottom to prevent deformation and cracking of 15X15cm span and Ø5mm section of steel wire. Each of the slabs was made with a different dosage, with 2 control concrete slabs with conventional aggregates, and 2 slabs with the application of SSS to replace part of the sand and a reduced amount of cement. The slabs were projected on a 12 cm thick cleaning concrete base with a spacing of 1 metre between them.



Figure 1: Distribution and measurements of experimental slabs

2.2 Mix proportions

Four concrete samples were manufactured to study the mechanical properties.

Table 1: Dosage of the concrete mixtures

		Dosage (Kg/m ³⁾												
	СЕМ	CG* 11/22	FG* 4/16	NS* 0/4	SSS 0-8	Additive (l)	Additive (2)	Water	Water added	Total weight	% total SSS application (SSS/Cem+Agg)			
HM-20 CR	250	560	500	1000	-	1.5	2.1	120	-	2430	0%			
HM20- EAI	230	560	500	750	280	1.5	2.3	120	6	2424	12%			
HA-25 CR	275	615	500	890	-	1.9	2.3	143	-	2423	0%			
HA25- EAI	265	615	500	705	205	1.9	2.6	143	4.4	2428	9%			

CG 11/22* Coarse gravel fraction 11/22mm; FG 4/16* Fine gravel fraction 4/16mm; NS 0/4* Natural sand 0/4mm



3. Experimental methods

3.1 Consistency of fresh concrete (UNE-EN 12350-2:2006)

The consistency of fresh concrete is the greater or lesser degree to which fresh concrete is able to deform and, as a consequence of this property, to occupy all the voids in the formwork or mould into which it is poured. The consistency is influenced by different factors, in particular the amount of mixing water, but also the maximum aggregate size, the shape of the aggregates and their granulometry.

3.2 Manufacture of specimens in situ for the determination of compressive strength UNE 83301:1991

The moulds for the production of test specimens were made of steel, 15 cm in diameter and 30 cm high. For compaction and moulding, a smooth, circular steel bar, 5/8" in diameter and 60 cm long with a rounded end, was used.

3.3 Sample extraction and compression test (UNE-EN 12504-1:2020)

The extraction and cutting operations must not disturb the adhesion between the mortar and the aggregates, so it is necessary that the concrete has sufficient strength to withstand these operations without altering its configuration (minimum 28 days). These extracted cores were tested for compressive strength at 28 and 90 days.

4. Results and discussion

4.1 Consistency of fresh concrete

The Abrams Cone was used to determine the consistency. It consists of filling a 30 cm high truncated coneshaped mould with fresh concrete. The decrease in height that occurs when the mix is demoulded is the measure that defines the consistency. Table 2 shows the consistency of each of the mixes used for the execution of the slabs.



	Table 2: Consistency			
-	Slump (cm)	Consistency (ECEHE 21)		
HM-20 CR	7	Soft		
HM-20 EAI	8.5	Soft		
HM-25 CR	9	Soft		
HM-25 EAI	9	Soft		

4.2 Manufacture of specimens in situ for the determination of compressive strength and extraction of samples for compression testing

From the 4 manufactured slabs, in-situ specimens were extracted and cured in the laboratory in a dry chamber at curing conditions of 100% humidity and 20°C temperature. These specimens were subjected to cracking at 7, 28 and 90 days. Subsequently, at 28 and 90 days after the execution of the slabs, the extraction of cores was carried out. The compressive strength test at 28 and 90 days was carried out on these extracted cores. Table 3 shows the results obtained.

 Table 3: Compressive strength (MPa) at 7, 28, 90 and 365 days of specimens manufactured on site and cores extracted in situ

 at 28 and 90 days.

	7 Days (MPa)	28 Days (MPa)		90 Days	s (MPa)	365 Days (MPa)	
	laboratory cured	laboratory cured	in situ	laboratory cured	in situ	laboratory cured	in situ
HA 25-CR	26.63	28.72	14.76	30.79	24.39	32	26.08
HA 25-EAI	27.31	28.84	18.31	36.08	24.79	36.84	27.87
HM 20-CR	20.23	21.98	19.79	22.85	22.39	23.47	24.26
HM 20 -EAI	21.92	22.97	13.56	26.59	18.64	27.08	23.74

The results obtained show a clear difference in values between the specimens cured in the laboratory at optimum conditions and the cores extracted on site; this variation is mainly due to the fact that the slabs were not thoroughly cured on site by irrigation and that the extraction of the cores did not achieve uniformity in the specimen, which showed remains of reinforcement leading to internal irregularities that affect the final compressive strength.

5. Conclusions

After analysing the results of this work, the following conclusions can be drawn:

- The behaviour of the stainless steel slag has been satisfactory in the substitution of sand in the percentages indicated.



- It is considered that with the substitutions carried out it is sufficient to not compromise the structural safety of the concrete.
- The percentage of sand substitution could be increased and a partial substitution of cement could be applied in accordance with the positive data obtained in the laboratory in relation to the compressive strength.

This work has demonstrated the viability of stainless steel slag, as substitution of aggregates, in terms of mechanical behaviour in concrete, which we consider to be a relevant advance in terms of the application of this waste and its future recovery.

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USE OF ALTERNATIVE SOLID ACTIVATORS WASTE-BASED IN ALKALI ACTIVATED MATERIALS FROM AGRI-FOOD RESIDUES

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Abstract

In recent years, geopolymers have emerged as alternatives to Portland cement so finding new waste-based activators for alkaline activation is an interest-growing area. This study focuses on utilizing two alternative solid activators: sodium silicate synthesized from both spent diatomaceous earth and waste glass. Mechanical properties of these materials were compared to those manufactured with conventional activators. Spent oil filtering earths, rich in aluminosilicates, were chosen as precursors for their sustainability. The alternative activators were synthesized through thermochemical processes and characterized using X-ray diffraction. Test specimens were prepared and subjected to mechanical testing after 28 days of ambient temperature curing. The use of solid alternative activators derived from spent diatomaceous earth and waste glass allowed for a one-part activation process and led to compressive strengths of 16.7 MPa and 35.8 MPa, respectively. In comparison, the use of commercial activators resulted in a compressive strength of 23.1 MPa.

1. Introduction

The construction industry is recognized as one of the most environmentally polluting sectors globally. Simply put, the production of Portland cement is responsible for approximately 6% of carbon dioxide emissions from fossil fuel sources. Therefore, finding an alternative to this material is strategically important in line with sustainable development goals. Alkali-activated materials or geopolymers are potential substitutes for Portland cement that are much more environmentally friendly. They can be synthesized from residues with high content of aluminosilicates or calcium oxides by adding an alkaline activator. However, it is worth noting that the activator itself contributes significantly to the carbon footprint of these materials, making the search for alternative activators an area of growing interest. Numerous studies have focused on the use of alternative activators [1], and some of them are based on the synthesis of alternative activators using this methodology has the advantage of producing solid activators, enabling the use of a one-part system, which offers several benefits [2]. Therefore, the investigation of alternative activators manufactured from residues holds promise for advancing in the field



of alkaline activation and providing viable alternatives to conventional chemical activators in the production of geopolymers.

2. Materials

2.1 Raw materials

To the purpose of this investigation three different residual raw materials were used: Spent Oil Filtering Earths (SOFE), Waste Glass (WG) and Spent Diatomaceous Earths (SDE). The conditioning of the residues was slightly different in every case due to the different nature of the residues.

SOFE and SDE, are wastes coming from agri-food industry processes so, first of all, they were subjected to a calcination treatment at 700 °C and 650 °C, respectively in order to remove the organic fraction. Later, each residue was ground in a ball mill, mainly with homogenization purposes. WG is an inorganic waste so it was directly ground in the ball mill. All raw materials were sieved under 0.100 mm prior to use them. Composition of the residues was determined by X-ray fluorescence (XRF) with a Zetium Malvern Panalytical equipment (United States) and it is shown in table 1.

Table 4. Chemical composition of residues used as raw materials.

Raw				Ch	emical (Compositi	on			
material	SiO ₂	Al_2O_3	Na ₂ O	Fe ₂ O ₃	K ₂ O	CaO	TiO ₂	MgO	P_2O_5	Other
SOFE	84.29	5.87	3.47	2.41	1.51	0.96	0.58	0.35	0.33	0.23
WG	73.93	1.0	12.12	0.42	0.71	10.59	0.04	0.51	-	
SDE	89.09	3.22	1.35	2.72	0.22	1.21	0.65	0.42	0.46	

2.2 Alkali activated materials manufacturing

Prior to the preparation of the alkaline activated materials, an alternative activator was synthesized using waste glass, WGA (43.57 g WG, 36.43 g NaOH and 20 g H₂O), and another one was manufactured from spent diatomaceous earth, SDEA (27.26 g SDE, 31.85 g NaOH and 40.89 g H₂O). The activators were designed to achieve an Ms value of 1 and were obtained by a thermal treatment at 300°C for 3 hours with a ramp rate of 10°C/min. Control samples activated with commercial activators (SOFE-COM) were created by mixing the precursor with an activating solution previously prepared from NaOH pellets (Panreac, 98% purity) distilled water and Na₂SiO₃ commercial solution (Panreac, 38.1 % wt, Ms=3.38).

Two more batches of samples were created to evaluate the potential of the alternative waste-based solid activators. SOFE-WGA samples and SOFE-SDEA samples were activated by using activators made from waste glass and spent diatomaceous earths, respectively. In all cases the addition of activator (commercial or alternative) was calculated to supply 20 g of Na₂O per every 100 g of precursor and Ms was set at 1 for every case of study as well. Total amount of water was added in a ratio of 0.9 g per every gram of precursor,



0.25 g per every gram of WG activator and 0.35 g per every gram of SDE activator to maintain constant the initial workability of the paste. Table 2 shows the exact composition of every batch, normalized for 100 g of precursor.

Sampla	Precursor (s)	NaOH (s)	Na ₂ SiO ₃ (aq)	$H_2O(l)$	WGA (s)	SDEA (s)
Sample	[g]	[g]	[g]	[g]	[g]	[g]
SOFE-COM	100	18.55	66.40	48.90	-	-
SOFE-WGA	100	-	-	100.71	42.85	-
SOFE-SDEA	100	-	-	104.65	-	41.86

Table 5: Designation and composition of mixtures.

Pastes were homogenised in a planetary mixer for 120 s and poured into prismatic moulds of 10x10x60 mm. The samples were preserved from evaporation for the first 24 h. At that point, the prototypes were demoulded and rest at ambient temperature until the age of test (28 days). No heat treatment was used during curing.

3. Results and discussion

3.1 Alternative activators characterization

Sodium silicate is known to have crystalline structure so the identification of the reaction products of the thermochemical synthesis process was carried out by this method. Figure 1 shows the results of XRD determination.



Figure 2: XRD study of alternative activators.



As can be seen in the diffractograms in Figure 1, the main reaction product of the heat treatment is sodium silicate, which is well known to have high activation potential.

3.2 Alkali activated materials characterization

Compressive strength was determined at the age of 28 days for all prototypes manufactured in accordance with the UNE-EN 1015-11:2020 standard and using a universal testing machine MST 8101 (100 kN) was utilized with a displacement rate of 2.0 mm/min.

Best result for compressive strength (35.8 MPa) is obtained when WG-based alternative activator is used. It is important to highlight that this result is equivalent to an improvement of around + 50 % in comparison with commercial activator. Diatomaceous earths activator however does not seem to be adequate enough and the compressive strength is significantly lower than using commercial solutions.



4. Conclusions

The SOFE residue appears to be a suitable residue to be used in the alkali activation process. Additionally, the alternative activator manufactured from WG demonstrated its effectiveness, resulting in superior mechanical properties (from 23.1 to 35.8 MPa) compared to the commercial activator what highlights the importance of exploring and optimizing the synthesis methods for these activators. It is worth noting that while the activator derived from SDE did not meet expectations in this study, it does not diminish the potential of other residues as viable sources for alternative activators. In fact, the results of this study are promising and suggest that alternative activation using residues via one-part will be strategic in the future development of these materials, contributing to a circular economy in different sectors and helping us to move closer to sustainable development goals.

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SPENT DIATOMACEUS EARTH AS AN ALKALINE ACTIVATOR IN THE MANUFACTURE OF ALKALINE CEMENTS

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Abstract

This work assesses the feasibility of the development of alkaline activated cements using spent diatomaceous earth (SDE) as a waste-based alternative activator for copper slags alkali-activated cements. The binders were obtained using copper slag as precursor and three different activation solutions prepared by mixing caustic soda with various amounts of spent diatomaceous earth. The results showed that materials activated with SDE reached higher compressive strengths than those activated with commercial sodium silicate. The study confirms the possibility of using SDE as an alternative and environmentally friendly source of silica in alkaline activation process.

1. Introduction

Portland cement is an indispensable building material. However, its manufacture involves the exploitation of quarries, high energy consumption and large amounts of emissions into the atmosphere [1]. For this reason, the study and development of new alternatives to Portland cement is priority research of great interest worldwide.

Alkaline-activated cements are green materials that considerably reduce CO_2 emissions without high economic cost. In addition, they have significant technical advantages over conventional cements. These are non-Portland cements based solely on natural minerals, industrial waste or by-products and an alkaline activator [2]. However, according to Tempest et al. [3], sodium silicate and sodium hydroxide activators cause most emissions and energy consumption in geopolymers. One example is sodium silicate, which is produced from natural resources (silicon and sodium carbonate) at high temperatures (1300 °C). For this reason, its production is energy intensive and generates CO_2 emissions into the atmosphere.

In this context, the purpose of this work was to investigate the possibility of using spent diatomaceous earth (SDE) and a sodium hydroxide solution as alternative sources to produce sodium silicate solutions in a more sustainable way. These SDE-based solutions have been proposed for the activation of copper slag (CS) to produce alkali-activated cements.



2. Properties of Materials

In this research, copper slags (CS) were used as a precursor of alkali activated cements. They were provided by Atlantic Copper S.A.U., located in Huelva (Spain). The by-product used to manufacture the alternative activator was spent diatomaceous earth (SDE), provided by the Heineken factory located in Jaén (Spain). Copper slags and diatomite were crushed in a ball mill and sieved to a particle size of less than 0.100 mm and 0.063 mm, respectively.

Chemical composition of raw materials was obtained by X-ray fluorescence (XRF) using a Philips Magix Pro model PW-2440 and are presented in Table 1. The slags were mainly composed of Fe_2O_3 (62.18%) and SiO₂ (27.65%). On the other hand, the main component of SDE is SiO₂ (89.09%).

Table 1. Chemical composition of raw materials (%w)

	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	SO_3
CS	27.65	2.04	62.18	1.25	0.38	0.03	0.63	0.56	0.21	0.04	0.90
SDE	89.09	3.22	2.72	1.21	0.419	-	1.35	0.217	0.653	0.464	0.0892

3. Experimental Methods

In this study, three different alternative alkaline solutions were prepared by mixing a solution of sodium hydroxide 10 M with different amounts of SDE. The mixture was kept at 80 degrees while stirring for 3 hours. Then, solid part was separated by filtration. Besides, control specimens with commercial activators were made using two different solutions: one made from sodium hydroxide solution (NaOH); and another one obtained by mixing equally sodium hydroxide and waterglass (SS). Composition of alkaline solutions is given in Table 2. Specimens prepared from alternative activators were named as SDE-*x*, where the *x* indicates the amount of SDE by each 100 ml of caustic soda solution (10 M). Control specimens prepared with commercial activators are designated according to the activator used, NaOH (NaOH) or sodium silicate/NaOH (SS) mixture.

Table 2. Alternative	e activators	composition
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NAME	SDE (g)	SS (g)	NaOH (g)	H2O (ml)
SDE-15	15	-	28.99	71.01
SDE-20	20	-	28.99	71.01
SDE-25	25	-	28.99	71.01
NaOH	-	-	28.99	71.01
SS	-	100	28.99	71.01



Copper slags were used as precursor of the alkali-activated cements. The liquid/solid ratio was kept constant at 0.35 obtaining a suitable workability. The fresh alkali-activated material was molded into 60x10x10 mm stainless steel moulds and subjected to 60 strokes on a Proeti shaking table to eliminate bubbles and achieve better compaction. Then pastes cured at room temperature for 24 hours, protecting them from evaporation with a plastic film cover. After this first curing period, they are demoulded and left in the air under atmospheric conditions until test day.

Physical and mechanical properties of the specimens were studied. The bulk density was determined according to ASTM 642-13 [4]. Flexural and compressive strength were obtained according to UNE-EN105-11 standard [5].

4. Results and Discussion

Bulk density values of samples activated with SDE were similar or slightly higher than those of the control specimens activated with commercial sodium silicate or sodium hydroxide (Figure 1). This may indicate the effective formation of denser reaction products when the waste-based alternative solution is used. Besides, all specimens slightly increased values with curing time, indicating a slight increase in the activation reaction.



Figure 1. Bulk density of the alkali-activated cements. Figure 1. Bulk density of the alkali-activated cements.

Regarding the mechanical properties, cements activated with spent diatomaceous earth reached higher compressive strength than those activated with commercial sodium silicate or sodium hydroxide (Figure 2). The highest compressive strength may be related to the highest amount of geopolymer gel and C-(A)-S-H gel formed, as well as to the increased bulk density, although the microstructure of the compositions must be investigated in the future. Furthermore, the compressive strength of all samples experienced a large increase with curing time. Best results were obtained by specimens with 25g of spent diatomaceous earth for every 100 ml of sodium hydroxide solution.





Figure 2. Compressive strength of the alkali activated cements.

Flexural strength increased as spent diatomaceous earth amount increased (Figure 3). However, obtained valuer were lower than those reached by those activated with commercial sodium silicate or sodium hydroxide. In most specimens, flexural strength increased with curing time, indicating an advance of the alkali-activated reaction.



Figure 3. Flexural strength of the alkali activated cements.

5. Conclusions

This study confirms the possibility of using spent diatomaceous earth as an alternative source of silica in alkaline activation process and a new path for the reuse and recovery of waste diatomaceous earth.

SDE-25 specimens showed promising results, reaching higher bulk density and compressive strength values to those manufactured with commercial sodium silicate. Although the flexural strength is lower than that obtained using the commercial activator, the decrease is considered admissible.

These results demonstrate that a cheaper and more environmentally sustainable technology can be used to produce sodium waterglass without thermal treatments, reducing the environmental impact of alkaliactivated materials.


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VALORIZACIÓN DE RESIDUOS DE CONSTRUCCIÓN Y DEMOLICIÓN JUNTO CON DIFERENTES SUBPRODUCTOS INDUSTRIALES A TRAVÉS DE MATERIALES DE ACTIVACIÓN ALCALINA

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Abstract

In this research, the synergy of valorising construction and demolition waste (CDW) together with the addition of three industrial by-products: chamotte (CHM), beer sludge (BS) and rice husk ash (RHA) has been studied, with the aim that these combinations of waste can be used as precursors in the manufacture of alkaline activated materials. For this purpose, four different mixes were made, one control (100CDW) and the rest substituting 40% by weight of CDW with the different industrial by-products, 60CDW-40CHM, 60CDW-40BS and 60CDW-40RHA. The same procedure has been followed for all of them and the same activator has been used, a solution of NaOH 8M (98 % purity) and Na2SiO3 (29.2 % SiO2) at 50 %. Once the specimens were manufactured, mechanical tests were carried out at 7 and 28 days of curing, obtaining compressive strengths of 15.2 MPa, 23.9 MPa, 37.8 MPa and 35.9 MPa for the 100CDW, 60CDW-40CHM, 60CDW-40BS and 60RCD-40RHA mixtures, respectively. These results demonstrate that it is possible to valorise CDW together with other industrial by-products as a precursor of alkaline-activating materials, obtaining an alternative binder to Portland cement, providing high mechanical strength and with a much lower environmental impact, thus contributing to a circular economy.

1. Introduction

Due to the fact that the manufacture of Portland cement has a high environmental impact (extraction of raw materials, high temperatures, greenhouse gas emissions). It is necessary to research and develop new, more optimised binders with similar properties but with a lower environmental impact. One of the most interesting is alkaline activated cement [1-4]. These materials are based on the chemical reaction of solid materials rich in amorphous silica and alumina (precursors), with varying amounts of calcium, activated with an alkaline solution (activator) at room temperature or slightly elevated [5-7]. This results in materials consisting of amorphous three-dimensional tetrahedral lattices of SiO4 and AlO4 with high thermal and chemical stability. Moreover, the precursors can be derived from natural sources or, more



interestingly, from industrial by-products, provided they have a suitable chemical composition [4].

In this investigation, the main by-product that is presented to be valued is (CDW). These are one of the heaviest and most voluminous waste streams, representing between 25-30% of all waste generated in the European Union. They are very heterogeneous and can contain any material that is part of a building or infrastructure (concrete, bricks, plaster, wood, glass, asphalt, excavated earth...) [8]. Most of said waste is deposited in landfills, generating a saturation problem with the consequent environmental impact. Likewise, most of the industries produce destination by-products whose majority is usually the landfill. To avoid this end, in this research different industrial by-products are used and their possible combination with CDW is studied in order to be used as precursors of alkaline activation cements.

Chamotte (CHM) is the material obtained by reducing the particle size of ceramic elements for construction. It is generated by failures in the sintering stage, which forms products with an inappropriate visual appearance, technological problems or deviations from geometric values, making their use unfeasible. Likewise, the beer sector generates high volumes of sludge (BS). It is estimated that for every hectoliter of beer produced, between 14 and 20 kg of sludge is generated which, in addition to its large volume, has an unpleasant smell and is therefore taken to landfills. Finally, as a by-product of rice, rice husk is obtained. Its degradation is a complex process, so it remains as residue, occupying large areas due to its low density, causing environmental problems. One method to reduce its volume is by combustion, obtaining an ash (RHA).

2. Properties of Materials

2.1 Materias primas

The industrial by-products, once received in the laboratory, are oven-dried to constant mass and, if necessary, calcined (BS at 750°C 4h). Both CDW and CHM have to be crushed and then ground, RHA only needs grinding because it has a very small particle size and finally BS does not need grinding or milling, since, after calcination, the particle size was suitable for sieving with a particle size of 0.100 mm. Subsequently, they are characterised using different techniques such as FTIR, XRD, SEM and XRF

Raw Material	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K2O	LOI
CDW	51.69	5.93	18.93	2.46	205	0.63	1.43	15.54
CHM	63.08	12.11	8.67	4.67	1.88	0.47	3.25	3.60
BS	17.41	0.98	52.36	2.28	1.49	1.42	0.24	17.54
RHA	73.60	-	0.78	0.28	0.72	0.14	1.63	20.83

Table 1: Chemical composition (XRF) of raw materials

2.2 Mix proportions

In Table 2, the dosages used for each mixture can be seen. First, a control mixture was made, only with CDW, and then 40% by weight of CDW was substituted by the rest of the by-products, so that the



influence of a silica-rich source (RHA), a calcium-rich source (BS) and a silica-alumina-rich source (CHM) on CDW can be studied. In all cases, the alkaline solution used was the same, 50 % wt NaOH 8 M and 50 % wt Na2SiO3, in order to obtain an activator modulus (SiO2/Na2O)=Ms=1). However, the required amount of activator was different depending on the by-product incorporated. The increase or decrease of the liquid/solid ratio, between the alkaline solution and the precursors, of the different mixtures is necessary to obtain a good workability.

Table 2: Chemical composition (XRF) of raw materials

Mix	CDW (g)	Other residue	Na2SiO3 (g)	NaOH (g)	H ₂ O (g)	Binder/ Liquid ratio	Ms
100CDW	400	-	80	19.69	60.31	0.40	1
60CDW-40CHM	240	160	90	22.15	67.85	0.45	1
60CDW-40BS	240	160	110	27.08	82.92	0.55	1
60CDW-40RHA	240	160	209	51.45	157.55	1.04	1

3. Experimental methods

3.1 Fabricación de los cementos activados alcalinamente

For the preparation of the alkaline activator, it is necessary to first obtain an 8M NaOH solution, and then add the necessary amount of Na2SiO3. Once the alkaline solution is obtained, it is left to cool at room temperature for 24 hours and pH measurements are taken. The mixtures of alkali-activated materials were prepared in a Proeti planetary mixer using the same sequence for all compositions. First, the dry raw materials, were mixed and homogenised for 90 s at low speed (140 ± 5 rpm) for 90 s. After this time, the activator solution was added to the homogeneous mixture and mixed at low speed for another 90 s. Subsequently, the walls of the container were stirred and the mixture was mixed again for another 30 s at high speed (285 ± 10 rpm). The workable pastes obtained were poured into stainless steel moulds to obtain prismatic samples ($1 \times 1 \times 6$ cm3) and subjected to 60 strokes on a Proeti shaking table to eliminate bubbles and achieve better compaction of the material. Then, the samples were covered with film to prevent the evaporation of water and thus allow the initiation of geopolymeric reactions, after 24 hours, they were demoulded and kept at room temperature (for de mixes 60CDW-40CHM and 60CDW-40BS) or at 60°C during 3 days (60CDW-40RHA) until the day of testing, 7 and 28 days.

3.2 Mechanical tests

Flexural and compressive strength was tested according to UNE-EN 1015-11:2000/A1:2007 [11] An MTS Insight 5 machine (5 kN capacity) with a dis-placement speed of 1.0 mm/min was used to determine the flexural strength. Five samples were tested to determine the average value of the flexural strength. A universal testing machine MTS 8101 (100 kN) with a displacement speed of 2 mm/min was



used to determine the compressive strength. Five halves from the flexural test are used to obtain the average value of the compressive strength.

4. Results and Discussion

4.1 Mechanical properties



Figure 1: Mechanical properties of alkaline activated materials. Compressive strength (left) and flexural strength (right).

The substitution of 40% by weight of CDW for the rest of the industrial by-products results in cements with higher mechanical compressive strength, except for the case of the 60CDW-40RHA mix after 7 days of curing, which, despite being the only one that requires a thermal curing process at 60°C for 3 days, the setting and hardening is very slow. However, when the curing time is increased to 28 days of curing, it can be observed that there is a notable increase in the compressive strength of the binary cements with respect to the control cements that use CDW as a pre-curing agent, increasing the compressive strength from 15.2 MPa for the 100CDW binders to 23.9 MP, 37.8 MPa, and 35.9 MPa for 60CDW-40CHM, 60CDW-40BS and 60CDW-40RHA cements, respectively. As for the flexural strength, the same trend continues, at early curing ages, 7 days, with all the industrial by-products, except with the 60CDW-40RHA mix, the flexural strength obtained for the 100CDW control binder is exceeded. However, when increasing the curing time to 28 days, the 100CDW control mix presents a flexural strength of 8.12 MPa, increasing to 12.65 MPa for the 60CDW-40CHM cements, maintaining with the incorporation of BS 60CDW-40BS, 8.06 MPa, and decreasing to 6.01 MPa for the 60CDW-40RHA cements

5. Conclusions

According to these results, the combination of CDW with different industrial by-products: chamotte, beer sludge and rice husk ash allows the valorisation of CDW. The maximum compressive strength is achieved with the binary cements 60CDW-40BS reaching 37.8 MPa, while, the maximum flexural



strength is achieved with the 60CDW-40CHM mix reaching 12.65 MPa.

Thus, the by-products of chamotte (CHM) and beer sludge (BS) can be highlighted, since, with their addition to CDW at 40% wt, they can be used as a precursor for the manufacture of alkaline-activated materials, notably improving both the compressive and flexural strength of cements that use only the CDW precursor. In addition, in both cases, curing takes place at room temperature, improving properties from very early ages and using a relatively low amount of commercial activator. However, the substitution of CDW by the RHA residue, although it improves the mechanical properties after 28 days of curing, its setting and hardening is very slow, requiring a thermal curing at 60°C for 3 days and the amount of activator needed is practically double that of the CHM and BS by-productsThus, these byproduct generating industries, whose ultimate goal is to seek profitability, recovery and avoid landfill, can find an effective and economically interesting alternative for the disposal of their waste by facilitating the reincorporation of these by-products, ensuring the protection of human health and the environment. Moreover, this allows for reuse, recycling and recovery, developing an alternative market for these wastes and promoting a circular economyIt can be stated that the manufacture of activated alkaline materials is a good option to add value to industrial by-products, giving rise to materials with high mechanical resistance values. In this way, society is offered a more sustainable option for the recovery of by-products generated in other activities and which, in many cases, would end up in landfill. This valorisation constitutes a unique opportunity for the development of new environmentally sustainable materials with properties comparable to those of Portland cement.

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MIXED RECYCLED AGGREGATES IN THE SUSTAINABLE ECO-CONCRETE INDUSTRY

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Abstract

The recovery of mixed recycled aggregates is currently a challenge for modern societies that pursue sustainable development and a circular economy model. This research work evaluates the technical and scientific feasibility of reusing the coarse recycled mixed fraction (50% and 75% by weight) as a granular skeleton of recycled eco-concretes, so that they can be proposed by technicians as a tool for increasing the sustainability of engineering projects. Physical (consistency) and mechanical (compression and splitting tensile strength) classifications were therefore carried out in the fresh and hardened state of the eco-concretes, respectively. The result of this work shows the feasibility of using this type of recycled aggregate in the design of concrete with a resistance of 25 MPa.

1. Introduction

Concrete is a ubiquitous material in society (~465 million of m³ in 2019 [1]). Globally it is also the most consumed human-made product, with widespread use in the construction of buildings, bridges, roads, and many other forms of infrastructure [2]. This fact characterises the concrete industry as having significant demand for natural aggregates, representing between 60-75% by volume of the average composition of a concrete [3].

In this context, together with the volume of construction and demolition waste (CDW) generated annually (~800 million tonne/year in the EU [4]) and the fact that most current regulations do not contemplate the use of so-called mixed recycled aggregates (MRA) as an alternative raw material in concrete manufacture [5] has intensified efforts in the scientific community in recent decades to assess the feasibility of using MRA as a new recycled raw material in this industry. The obtained results in previous researches [5-10] shown that the incorporation of this recycled coarse fraction in low percentages (<50%) of MRA could be to use as alternative to the natural aggregates in the design structural concretes with a characteristic strength to compressive ≤ 25 MPa.

The objective of this research is to evaluate the effect of the partial incorporation (50% and 75%) of mixed coarse aggregate as a granular skeleton in the formulation of eco-recycled concretes with a lower carbon footprint during its manufacturing process. A previous classification of the MRA was therefore



carried out to later determine the consistency in the fresh state, the mechanical properties (compression and splitting tensile strength) and ultrasound pulse velocity in the hardened state of the new sustainable eco-concretes.

2. Properties of Materials

- Cement: CEM I 52.5 R that meets the requirements indicated in the European standard EN 197-1 [11].
- Natural aggregate: siliceous aggregate from crushing that comes in two granulometric fractions: natural sand (Ar_{NA}, 0/6 mm) and natural medium gravel (Gv_{NA}, 6/12 mm).
- Recycled aggregate: coarse mixed recycled aggregate (Gv_{MRA}) from the ARAPLASA CDW management plant, located in Plasencia, Spain, with a maximum and minimum size of 12 mm and 6 mm, respectively. This aggregate consists mainly of unbound aggregates (Ru), concrete (Rc) and ceramics (Rb) by ~44%, ~28% and ~24% by weight, respectively.

Table 1 shows the mechanical and physical properties of the aggregates (recycled and natural) used in this investigation, together with the limits required for the aggregates used in the manufacture of structural concretes according to the Structural Code (CodE) [12]. In it, it is observed that the only property that does not meet current requirements is water absorption. This higher value is directly associated with the intrinsic characteristics of the components (Rc and Rb, mainly) present in the MRA.

- Superplasticiser: ViscoCrete®-90 NG, supplied by Sika®.
- Betacarbonate: natural calcium carbonate with $CaCO_3 \ge 98.5\%$.
- -

Table 1: Properties of the aggregates.

Property	Gvmra	Gvna	Arna	CodE [7]
Density (kg/m ³)	2.66	2.78	2.82	-
Water absorption after immersion for 24 h (wt.%)	7.69	0.88	1.18	≤5
Los Angeles coefficient (wt.%)	40	16	-	≤40
Flakiness index (wt.%)	15.48	20.36	-	<35
Sand equivalent	-	-	73	>70

3. Experimental methods

The experimental programme includes the design and manufacture of a total of three mixtures (M1, M2 and M3), using the Faury dosage method for its design, setting the objective of obtaining eco-concretes with a characteristic resistance (f_{ck}) of 25 MPa and exposure classes X0 and XC. Table 2 shows the dosing results of the concrete mixes.



Component (leg/m ³)		Mixes	
Component (kg/m ⁻)	M1	M2	M3
Natural sand	658.65	658.65	658.65
Natural medium gravel	992.26	496.13	248.06
Recycled medium gravel	0.00	433.55	650.32
Betacarbonate	20.37	20.37	20.37
Cement	318.50	318.50	318.50
Water	190.10	215.01	227.47
Admixture	2.96	2.96	2.96
Note: M1: conventional concrete; M2	concrete with 50% MI	RA; M3 : concrete wit	th 75% MRA.

Table 2: Dosages of the concrete mixtures.

Finally, the eco-recycled concretes were classified by determining the workability pursuant to the EN 12350-2 standard [13], the compressive strength at 28 days pursuant to EN 12390-3 [14], the tensile strength at 28 days of curing pursuant to EN 12390-6 [15] and ultrasonic pulse velocity (UPV) at 28 days pursuant to EN 12504-4 [16].

4. **Results and Discussion**

Table 3 shows the results of the properties evaluated in the concrete in its fresh and hardened state. Regarding the consistency according to the Abrams cone, it is observed that all the mixtures, regardless of their composition, present a soft consistency (50-90 mm).

Duonoutru		Mixes	
Property	M1	M2	M3
Consistency (mm)	54 ± 3	55 ± 3	55 ± 3
Compressive strength at 28 days	45.65 ± 0.21	38.55 ± 0.07	36.85 ± 0.35
Splitting tensile strength at 28 days	2.98 ± 0.19	3.01 ± 0.06	3.24 ± 0.15
Ultrasonic pulse velocity (m/s) at 28 days	4424.58 ± 66.56	$4227.67 \pm 101,60$	4069.67 ± 68.20

Table 3: Properties of the concretes.

Regarding compressive strength, the following was observed: i) the average strength at 28 days was higher than the target strength ($f_{ck}=25$ MPa); ii) there was a loss with the percentage MRA addition, registering a decrease in M2 and M3 of ~16% and ~19% with respect to M1, as previously observed by Cantero et al. [6]; and iii) the drop experienced was much lower than the addition percentage. Regarding tensile strength, it can be seen that the M2 and M3 mix have resistance equal to or greater than M1. This good behaviour is associated with the intrinsic properties of the MRA/paste interfaces (ITZs), as previously found by Sáez del Bosque et al. [7].

Finally, the UPV results show that MRA addition does not affect the quality of the concretes, all of which are classified as good quality (3660 m/s \leq UPV \leq 4575 m/s).



5. Conclusions

The conclusions based on the results obtained are:

- The addition of 75% mixed recycled aggregate does not cause a loss of workability in the new recycled eco-concrete.
- The compressive strength presents a decrease much lower than the addition percentage.
- The addition of MRA causes the tensile strength of the eco-concretes to be equal to or greater than that of the reference concrete.
- In light of the mechanical performance of the newly designed recycled concretes, they could be used for structural purposes ($f_{ck} = 25$ MPa).
- The addition of MRA does not affect the quality of the concrete according to the ultrasonic pulse speed.

Finally, it should be noted that the results obtained will contribute to including this type of aggregate in the current regulations, which would mean a great advance in construction and demolition waste recycling and converting the current linear model to a circular model.

6. Acknowledgements

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MIXED CONSTRUCTION AND DEMOLITION WASTE AS A COMPONENT OF COATING ECO-MORTARS

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Abstract

At this time, the construction sector and materials manufacturers are immersed in a conversion process from a linear production model to a circular model, so as to reduce the carbon footprint in final products and use energy more efficiently. Motivated by this reality, this research pursues the formulation of new eco-mortars for protection and coating incorporating mixed recycled construction and demolition waste as a constituent part of its granular skeleton. To achieve this objective, different physical and mechanical properties of the formulated eco-mortars were evaluated. Finally, the results show that there these new recycled raw materials can be used in the design of these new eco-mortars.

1. Introduction

The construction sector as a whole is responsible for 50% of extracted material [1], 40% of global energy consumption and 16% of global water consumption [2]. Associated with this activity is the generation of so-called construction and demolition waste (CDW), which, according to a recent report, the EU-27 generates ~374 Mt annually, which represents 35% of the solid waste generated per year [3]. Recycled aggregates from CDW management can be classified mainly into two large groups: i) recycled concrete aggregates; and iii) mixed recycled aggregates that represent 67% of the total volume [4].

Mixed recycled aggregates are characterised by their compositional heterogeneity, which is a barrier to recovering them. This fact is accentuated in the fine fraction <4 mm, which represents, depending on the technological process used in the CDW plant, 40% of the total recycled aggregate produced [5].

In this context, the objective of this research is to completely replace the natural fine aggregate with a mixed recycled fine aggregate in the optimal formulation of a new eco-mortar for protection and coating. To achieve this, an initial classification was carried out on the aggregates and later the physical properties (bulk density and consistency) and mechanical properties (compression and flexural strength) were determined in the fresh and hardened state, respectively, of the formulated mixtures.



2. **Properties of Materials**

In this research, two mixtures with different granular structure were formulated and subsequently evaluated. The materials used are organised into three large groups: i) binder (cement); ii) mineral that make up the granular skeleton (calcium hydroxide, metakaolin, natural sand, mixed recycled sand and lightweight aggregates); and iii) other components (fibres and additives).

The cement used was ordinary Portland cement CEM I 42.5R that meets the requirements of the European EN 197-1 standard [6]. The aggregates used were subjected to a screening process to be able to work with the fraction less than 2 mm. In mix A, natural crushed greywacke sand (0/6 mm) with a 2.99 kg/dm³ apparent density was used, while for mix B, recycled sand (0/6 mm) from mixed CDW from the ARAPLASA waste plant in the north of Cáceres, Spain, was used. This recycled sand has an apparent density lower than natural sand, 2.70 kg/dm³, and is mainly made up of concrete components (~44% by weight), unbound aggregate (~43% by weight) and ceramic material (~11% by weight). Regarding the light aggregates, perlite and vermiculite with a maximum size of 2 mm have been used.



Figure 1: Mix A and Mix B composition.

Figure 1: Mix A and Mix B composition.

Finally, Figure 1 shows the composition of the mix as a percentage by weight of each of the components that make up the new environmentally-friendly mortars. It is important to clarify that for these mixtures, a water/solid ratio of 84% was selected.

3. Experimental methods

The tests carried out on mixtures A and B began with a physical classification of the powder mixtures using the granulometry method according to the EN 1015-1 [7] standard, by dry sieving. After mixing,



the fresh bulk density tests regulated by the EN 1015-6 [8] standard and the run-off test according to the EN 1015-3 [9] standard were carried out using the shaking table method to in order to evaluate the physical properties. Finally, the 4x4x16 cm prismatic test tubes (three test tubes/mixture and age at break) manufactured are subjected to the bending and compression test regulated in the EN 1015-11 [10] standard to assess their mechanical properties at the age of 7 and 28 days.

4. **Results and Discussion**

The granulometry test for mixtures A and B reveals that they have a size of less than 4 mm and continuous curves. It was also observed that $\sim 27\%$ and $\sim 30\%$ by weight are made up of particles smaller than 0.080 mm, these values being in the optimal theoretical range of fines (24-35%) for the granular skeleton of this type.

Table 1 shows the values of the physical and mechanical properties of the tested mortars. The run-off values of the eco-mortars studied can be classified as plastic mortars (140-200 mm) pursuant to EN 1015-6 [8], with Mix B experiencing a ~3% decrease compared to Mix A due to the addition of mixed recycled aggregates, as previously perceived by Miranda et al. [11]. Regarding the apparent density, Mix B is lower ($\Delta \rho_{mix B} \sim 1.3\%$ compared to mix A) associated with the lower density of a recycled aggregate with respect to natural aggregate due to its more porous micro-structure.

Table 1: Test results for mixture A and B.

	a	Bulk	М	echanical pro	properties (MPa)			
Mix	Consistency	density (kg/m ³)	Compressive strength Flexural strength		strength			
(mm)	(mm)	(kg/m)	7 days	28 days	7 days	28 days		
Mix A	166.77	643.42	0.21	1.24	0.14	1.11		
Mix B	161.64	635.06	0.30	1.02	0.18	1.01		

Finally, Table 1 shows that the addition of mixed recycled aggregate in Mix B translates into a decrease in mechanical properties compared to Mix A, registering a performance loss for flexural and compression strength at 28 days of \sim 9% and \sim 17% compared to Mix A. This decrease is much lower than the addition percentage, as previously observed by Silvia et al. [12].

5. Conclusions

The following conclusions can be drawn from this research work:

- The granulometry reveals that both mixtures are continuous and have a maximum size of 2 mm, with a percentage of fines within the established ranges.
- The addition of mixed recycled aggregates does not cause a significant decrease in the bulkdensity and consistency of eco-mortar B (Mix B).
- The mechanical performance shows a decrease due to the addition of the mixed recycled granular skeleton of CDW, being lower than the addition percentage.



The eco-mortars could be used as protection and coating mortars, although a second phase of tests is required in which the elastic, acoustic, water absorption and thermal conductivity properties are analysed.

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CONSTRUCTION AND DEMOLITION WASTE REUSE IN THE ECO- CONCRETE INDUSTRY

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Abstract

Despite the progress made in recent decades in recovering construction and demolition waste in the concrete industry, intense training and awareness work among technicians and professionals in the sector is still needed. This research work addresses the classification of a recycled concrete aggregate and subsequent design and formulation of an eco-concrete with a 25% coarse and fine recycled concrete fraction, evaluating its physical, mechanical and impermeability properties against water. As a result, a recycled eco-concrete with optimal mechanical properties and a porous impermeable structure is obtained, which would logically make it suitable for use as structural concrete with a characteristic design strength of less than and equal to 30 MPa.

1. Introduction

Concrete products are second only to water as the most-consumed material in the world by mass, with an estimated yearly consumption approaching 30 billion tonne, which leads to per capita production greater than that of any other material [1]. This concrete industry is responsible for annual consumption of approximately 1.35 billion tonne/year [2].

This scenario, together with the need to increase CDW recovery rates and include the use of recycled concrete aggregates (RCA) within practically all the regulations for concrete structures, requires continued work on knowledge and research into the formulation of new eco-concretes that exceed the maximum limit established by the regulations of each member state (i.e. according to the Spanish Structural Code (CodE) 3] the maximum threshold is 20% of the coarse fraction of concrete).

This work aims to consolidate and advance scientific knowledge of the feasibility of the use of recycled concrete aggregates in the design and formulation of eco-concretes for structural purposes within construction projects. An incorporation percentage of 25% of recycled aggregate was therefore established, subsequently evaluating its effect on the physical properties (consistency and entrained air content) in the fresh state and mechanical properties (compression and tensile strength) and durability (maximum depth and average water penetration under pressure).



2. **Properties of Materials**

The recycled aggregates were supplied by the ARAPLASA CDW processing plant located in Plasencia, Cáceres, Extremadura. These aggregates are classified into three granulometric fractions: 0/6 mm recycled sand (Ar-RCA), 6/12 mm recycled gravel (Gv-RCA) and 12/20 mm recycled gravel (G-RCA). At a compositional level, both fractions are characterised by a concrete (Rc), unbound aggregate (Ru) and ceramic (Rb) content of ~51%, ~47% and ~2% by weight, respectively, being classified as concrete recycled aggregates (RCA). Natural aggregates are siliceous crushed aggregates, presented in three granulometric fractions: natural sand (Ar-NA, 0/6 mm), medium crushed stone (Gv-NA, 6/12 mm) and coarsely crushed stone (Gv-NA, 12/20 mm).

Table 1 shows the physical and mechanical properties of the aggregates used (natural and recycled), aswell as the maximum thresholds allowed pursuant to the Structural Code (CodE) [3].

PROPERTIES	G-RCA	Gv-RCA	Ar-RCA	G-NA	Gv-NA	Ar-NA	CodE
Density (kg/dm ³)	2.69	2.73	2.89	2.77	2.78	2.82	-
Water absorption (wt.%)	4.49	6.81	7.99	0.78	0.88	1.18	$\leq 5 \text{ or } \leq 7$
Flakiness index (wt.%)	7.74	7.58	-	24.79	20.36	-	<35
Los Angeles coefficient (wt.%)	32	28	-	18	16	-	≤40
Sand equivalent	-	-	57	-	-	73	>70

The Portland cement used is a CEM I 42.5 R that meets the requirements established in the European EN 197-1 standard [4]. It was supplied by the Lafarge Holcim group plant in Villaluenga de la Sagra, in the Spanish province of Toledo, Spain.

Finally, the superplasticiser used in the concrete manufacture is FUCHS BRYTEN NF, supplied by FUCHS Lubricantes S.A.U.

3. Experimental methods

3.1 Concrete manufacturing

Table 2 shows the composition of the mixtures resulting from the dosage process described in the previous paragraph: i) reference concrete with 100% natural aggregate (M1); and ii) recycled concrete with 25% by weight of coarse recycled concrete aggregate (M2).



Table 2: Mix batching

Components (kg/m ³)	Ν	11 ^{Mix concrete} M2
Natural sand (0/6 mm)	732.36	540.60
Medium crushed stone (6/12 mm)	382.96	282.69
Coarsely crushed stone (12/20 mm)	766.69	565.94
Recycled sand (0/6 mm)	0.00	168.84
Recycled medium crushed concrete (6/12 mm)	0.00	90.29
Recycled coarsely crushed concrete (12/20 mm)	0.00	184.18
Cement (CEM I 42.5 R)	400.00	400.00
Water	193.03	212.52
Superplasticiser	6.20	6.20
Note: *Dosage method used: Mix British Method	[5]; **fck=30 M	Pa and XC environmental exposure

3.2 Concrete classification

The formulated concretes were classified by determining the workability [6] and entrained air [7] in the fresh state and the compression [8] and splitting tensile [9] strength and water penetration under pressure [10] at 28 days.

4. **Results and Discussion**

4.1 Fresh concrete properties

Table 4 shows the results obtained from the properties analysed in the concrete in its fresh state. Regarding the consistency, it is observed that the addition of recycled aggregate does not cause a workability loss in the new concrete (M2), finding the value obtained within the range 60-90 mm corresponding to a soft consistency, pursuant to the CodE [3].

Property	M1	Mix concret _{M2}
Consistency (mm)	73 ± 4	70 ± 5
Entrained air (vol.%)	1.83 ± 0.02	2.10 ± 0.01

Table 4: Physical properties of mix concrete in fresh state

Regarding the entrained air, it is observed that the inclusion of materials from construction waste causes an increase with respect to the use of natural aggregates, mainly due to the lower density and greater porosity of the new recycled aggregates [11].



4.2 Hardened state properties

Table 5 shows the results of compressive and splitting tensile strength of the concrete at 28 days, as well as the average and maximum penetration depth of water under pressure. Regarding the compressive strength, the value obtained for concrete M1 and M2 is higher than the characteristic design strength of 30 MPa. It is also highlighted that regardless of the mechanical property evaluated, there is a decrease with the addition of recycled concrete aggregate due to the more porous structure of the recycled aggregates that have a layer of mortar adhered to them and the presence, with a greater or lesser frequency, of micro-cracks resulting from the CDW management technological process [12].

Properties	M1 ^{Min}	x concrete M2
Compressive strength (MPa)	50.20 ± 0.56	44.41 ± 0.75
Splitting tensile strength (MPa)	4.02 ± 0.08	3.50 ± 0.15
Mean depth of penetration of water under pressure (mm)	5	9
Maximum depth of penetration of water under pressure (mm)	15	14

Table 5: Properties of the mix concrete at 28 days

Finally, regarding the maximum depth and mean penetration depth values, it can be seen that regardless of the type of concrete (M1/M2), the values are lower than the maximum limit (mean depth \leq 30 mm and maximum depth \leq 50 mm) required by the CodE [3]. Therefore, the addition of RCA makes it possible to achieve an eco-concrete with a porous structure that is sufficiently impermeable to water.

5. Conclusions

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

- The substitution of partially recycled aggregate for natural aggregate does not significantlyaffect the properties of the new eco-concrete in the fresh state.
- The compressive and tensile strength of eco-concrete M2 is approximately 12% lower than M1,this decrease being much lower than the replacement percentage.
- Recycled concrete has a compressive strength greater than the design strength (f_{ck} =30 MPa).
- The addition of recycled aggregate does not negatively influence the water impermeability of the eco-concrete, meeting the requirements established by the CodE.

As a general conclusion, it can be established that recycled eco-concrete could be used for the design and execution of concrete elements with $f_{ck} \leq 30$ MPa, although the durable behaviour of this new family of concretes first needs to be verified.



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CONCRETE WITH RECYCLED AGGREGATES BEYOND THE CODE

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Abstract

The use of construction and demolition waste (CDW) is a common practice worldwide. The valorization of this waste is one of the European priorities, considering its use preferential since the 90s. The present researchs shows the possibility of expanding the use of recycled aggregate above the conservative 20% proposed by Spanish regulations. The compressive strengths obtained in recycled concrete are lower than those of their respective references, however results evidenced a small decreasing in this parameter (15% for replacements greater than 40% of coarse aggregate).

1. Introduction

Obtaining recycled aggregates from construction and demolition waste is a common practice, based on the large volume of this type of waste produced and its technical and economic feasibility. Subsequently, the recycled aggregates obtained can be incorporated as granular material in backfilling and leveling, as materials treated with hydraulic binders in pavements and leveling, prefabricated mass concrete elements, or in roller-compacted concrete, among others [1].

The structural concrete instruction (EHE 08) [2] already included two annexes regulating the use of recycled aggregates in concrete production, based on the research carried out in the RECNHOR project (2004). Currently, article 20.8 of the Structural Code (SC) [3] establishes the framework for this type of aggregate to manufacture structural concrete, setting stringent limits that can be described as conservative. The SC only allows the use of recycled coarse aggregate, limits the percentage of replacement of natural aggregate by recycled aggregate to 20%, and only considers it for the manufacture of mass and reinforced concrete (it is not allowed for prestressed concrete) with a characteristic strength of up to 40 N/mm2. This standard also limits the origin of recycled aggregates for concrete, as they must come from waste generated when demolishing healthy and high-strength concrete structures, and, additionally establishes the physical-mechanical requirements they must meet.

On the other hand, there is currently research in which these percentages of replacement of natural aggregate by recycled aggregate are exceeded. Recycled products also replace the fine fraction of the aggregate, and mixtures are designed to obtain high-strength, self-compacting concrete or alkaline-activated mortars [4-6].

However, the present work aims to establish the possibility of significantly increasing the replacement percentages of recycled aggregate in concrete commonly used in most construction works, such as mass concrete (HM-20) and structural concrete (HA-25). Usually, many of these types of concrete are used and



increasing the use of recycled aggregate in their composition will align the construction industry with the Sustainable Development Goals, specifically contributing to achieving SDG 12 and 13.

2. Materials and methods

CEM II/B-M (QL) 42.5R cement, crushed aggregates from a nearby quarry, and superplasticizer additives were used for the dosing of the reference concrete. Table 1 shows the dosage of the two reference concrete. In this work, the effect of substituting several percentages of different coarse aggregate fractions (AG 4/11 and AG 10/20) will be studied. The recycled aggregates came from an inert waste plant (AG 4/11 and AG 11/22), and their bulk density and absorption values were 2670 and 2680 kg/m3 and 6.3% and 3.5% respectively. Figure 1 shows the particle size of natural aggregates (N) and recycled aggregates (R).



Figure 1. Particle size of natural aggregate (N) and recycled aggregate (R).

The recycled aggregates come from a construction and demolition waste treatment plant, where the waste is subjected to various processes until the required particle size is obtained. This research used recycled aggregates with grain size fractions of 4/11 and 11/22mm. 6 different dosages were carried out to study the behaviour of these concrete. The effect of increasing the percentage of aggregate substitution from 20% to 60% was studied, and the influence of pre-immersing the recycled aggregate in water was

also studied to saturate it and prevent it from absorbing mixing water. Table 1 shows the dosages used.

3. Results

Different properties as slump, density in the fresh and the hardened states, and air content were measured following the corresponding European standards [7-10]. The obtained results are summarized in Table 2. Subsequently, the hardened concrete was tested for water penetration under pressure and compressive strength [11,12]. The Structural Code [3] indicates that in case of structural elements located in very aggressive environments (XS, XD, XF, XM or XA), the concrete must present a sufficiently impermeable



behaviour, determined according to UNE EN 12390-8 [11] with the modifications and criteria to check the conformity of section 57.3.3. With this criterion, the requirement of the permeability condition would only apply to reinforced concrete in aggressive environments. In the present work, the test has been carried out on concrete with coarse aggregate substitution percentages of 20, 40 and 60 %.

The results can be seen in Table 2. According to the Table 43.3.3 of Structural Code specifications [3], these penetration values would be acceptable in most of aggressive environments.

	Natu	Natural Aggregate (N) Recycled Aggregate (R)								
	AF 0/4	AG 4/11	AG 10/20	AG 4/11	AG 11/22	Cement	Additive	Water	w/c	
	[kg]	[kg]	[kg]	[kg]	[kg]	[kg]	[kg]	[1]	[-]	
Reference										
HM 20	980	225	775			230	3	190	0.83	
HA 25	960	210	775			280	3.7	190	0.68	
20% R										
HM 20	980	180	620	43.4	150	230	3	196	0.85	
HA 25	960	168	620	40.5	150	280	3.7	196	0.7	
40% R										
HM 20	980	135	465	86.8	299.9	230	3	201.9	0.88	
HA 25	960	126	465	81	299.9	280	3.7	201.6	0.72	
60% R										
HM 20	980	90	310	135	465	230	3	207.9	0.9	
HA 25	960	84	310	126	465	280	3.7	207.5	0.74	

Table 1. Dosages with different percentages of coarse aggregate replacement

Table 2.	Air content.	slump.	density	/ and de	pth i	penetration	results
	/	S.G. (1)				o circeraero ri	

	Replacement	Air content	Slump	Fresh Density	Hard Density	Depth
	[%]	[%]	[mm]	[kg/m ³]	[kg/m ³]	penetration [mm]
Reference						
HM 20	0	1.7	80	2425.7	2378.0	44
HA 25	0	1.8	70	2422.2	2386.1	36
20% R						
HM 20	20	1.9	90	2395.7	-	69
HA 25	20	2	110	2370.9	-	33
40% R						
HM 20	40	2.4	120	2410	2342.8	66
HA 25	40	2.3	150	2381.9	2324.8	33
60% R						
HM 20	60	2.3	80	2402.7	-	88
HA 25	60	2.4	90	2361.8	-	62



Cylindrical specimens of 150 x 300 mm were prepared from each of the manufactured mixtures to determine the compressive strength at different curing ages. Figure 2 shows the results of compressive strength at 7 and 28 days with different types and different percentages of replacement of natural aggregates by recycled aggregates for HM20 mass concrete and HA 25 structural concrete.



Figure 2. Compressive strength at 7 and 28 curing days of HM20 and HA25 concrete.

An apparent reduction in compressive strength is detected as the percentage of recycled aggregate used increased, although for all dosages, even with the coarse aggregate content equal to 60% of the coarse fraction 4/22, average strengths compatible with the characteristic strength required for HM20 and HA25 concrete are still achieved. The reductions in the strength of the reference concrete reached a maximum value of 18%.

4. Conclusions

The conclusions that can be drawn from the work carried out are as follows:

- All the dosages used present good workability compatible with the placement of these concrete.
- The density of the concrete is slightly reduced, in line with the lower density of the recycled aggregate.
- The compressive strengths obtained in recycled concrete are lower than those of their reference concrete. The decrease in strength can exceed 15% for replacements of more than 40% coarse aggregate.
- The water permeability values indicate that using recycled aggregate increases the risk of penetration of aggressive agents. Nevertheless, values close to the reference concrete are maintained, provided the dosage is carried out appropriately.
- Substitution levels higher than those allowed in the instruction seem feasible, and 40 or even 60% can be reached in some cases, moderate in terms of durability.



5. Acknowledgements

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CARACTERIZACIÓN DE LA ESCORIA BLANCA DE ACERÍA PARA SU UTILIZACIÓN COMO ADICIÓN MINERAL EN CEMENTOS MIXTOS

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Resumen

Cada vez se presta más atención a evitar el vertido de escorias de horno de cuchara (LFS) procedentes de la siderurgia secundaria debido a su potencial reciclabilidad/utilización tras un proceso de valorización. En este trabajo experimental se utiliza una escoria blanca española como remplazo de cemento en morteros en proporciones desde 0 hasta el 75%. La escoria blanca presenta compuestos cristalinos reactivos, inertes y potencialmente expansivos (MgO). La escoria afecta los tiempos de fraguado, reduciéndolos, como también generando una merma en la resistencia a compresión. A pesar de los efectos negativos, en cantidades del 25% y del 50% es posible utilizar la escoria como adición mineral en combinación con el cemento Portland.

1. Introducción

El progreso industrial en curso y la creciente preocupación socioambiental obligarán a la industria de la construcción a adaptarse en relación al cambio climático y, por lo tanto, modificarse. Hoy en día, una gran cantidad de residuos industriales no se valorizan y se depositan en vertederos como residuos, sin contribuir a una industria orientada a la economía circular.

Las industrias del cemento y el hormigón son importantes fuentes de emisión de gases de efecto invernadero e intensivas en el consumo de recursos naturales. Se calcula que la producción de cemento es responsable del 5-8% de las emisiones totales de CO2 [1]. Asimismo, la industria siderúrgica presenta un crecimiento significativo de la producción y seguirá en aumento durante las próximas décadas. Las tendencias de producción se inclinan hacia la ruta del horno de arco eléctrico (EAF), debido a la posibilidad de reutilizar la chatarra. Esta ruta genera principalmente dos residuos: La escoria de horno de arco eléctrico y la escoria blanca de afino o LFS, por sus siglas en inglés (ladle furnace slag) [2].

La LFS es un residuo potencial de ser valorizado debido a sus propiedades físicas, composición química/mineralógica y afinidad con los materiales de base cemento. En la actualidad, se producen cerca de 20 a 50 kg de LFS por tonelada de acero. Sin embargo, debido a barreras tecnológicas en su proceso de valorización (baja actividad cementante y problemas de inestabilidad de volumen), su destino final es ser depositado en vertederos [3].

En este trabajo se caracteriza una escoria de acería y se identifican las posibilidades de su uso como adición mineral para generar cementos mixtos, desde el punto de vista mecánico y de inestabilidad volumétrica.



2. Materiales y metodología

En este trabajo se utiliza cemento portland CEM I 52,5R, con una densidad de 3100 kg/m3, árido fino natural (0/4mm), de origen calizo, con una densidad de 2660 kg/m3 y una absorción de 1,1%. El árido fino presenta una distribución continua de partículas, donde el 98% del material pasa por el tamiz de 4mm y con un 8% de material que pasa por el tamiza de 0.063mm. El módulo de finura del árido es de 3.0. Igualmente se utiliza una escoria blanca producida en España (LFS) con un tamaño de partícula menor a 75 micras y una densidad de 2910 kg/m3

La composición química (Tabla 1) de la escoria blanca y del cemento son similares y presentan los mismos compuestos mayoritarios, a saber: Ca, Si y Al. En menor cantidad se observa el Fe, Mg y S. La composición mineralógica de la escoria está comprendida por β -C2S, mayenita, periclasa, portlandita, brucita, calcita, γ -C2S, gelenita, merwinita y wustita. Se debe señalar la complejidad mineralógica de la escoria, como también la presencia de MgO y la ausencia de CaO.

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Elemento	CaO	SiO2	Al2O3	Fe2O3	MgO	SO3	Otros	PPC
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
CEM	63.3	18.7	4.7	3.3	1.5	3.1	1.6	2.6
LFS	41.5	25.5	5.8	4.3	5.5	2.6	2.0	12.8

Tabla 1: Composición química del cemento y la escoria blanca

La influencia de la escoria en combinación con cemento se determina en pastas y morteros, utilizando la escoria blanca como remplazo del cemento. Se fabrican morteros estándar con 25, 50 y 75% de escoria blanca remplazando el cemento, en peso. La relación agua/cementante se mantuvo en 0,5 y la relación arena a cementante es de 3. Con el fin de mantener la consistencia de los morteros un aditivo plastificante se utiliza en diferentes proporciones en relación al peso del cemento (Pozzolith 7003). Las dosificaciones estudiadas se muestran en la Tabla 2. Los morteros se fabrican según la norma UNE EN 196-1 y las probetas de los diferentes tipos de morteros se curan en cámara húmeda (95% H.R. y 22°C) hasta la fecha de ensayo (7, 28 y 90 días).

Tabla 2: Dosificació	de los morteros	con escoria blanca
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Mortero	Cemento (g)	Agua (g)	Arena (g)	Escoria (g)	Plast. (%)
Control	450	225	1350	0	0.5%
75C + 25LF	337.5	225	1350	112.5	0.8%
50C + 50LFS	225	225	1350	225	1.3%
25C + 75LFS	112.5	225	1350	337.5	1.6%

El tiempo de fraguado se determina siguiendo la norma UNE EN 196-3. También se estudian las reacciones iniciales de hidratación por medio de calorimetría semi-adiabática, realizada hasta las 150 horas.



Finalmente, la estabilidad volumétrica se estudia utilizando probetas prismáticas de 25*25*265 mm y siguiendo las especificaciones de la norma ASTM C490.

3. Resultados y discusión

La figura 1 muestra el comportamiento de las pastas con los diferentes contenidos de escoria. Se puede observar que el tiempo de fraguado del cemento está comprendido entre los 200 minutos (inicio de fraguado) y los 310 minutos (final de fraguado). Cuando se incorpora la escoria blanca se observa un aumento del tiempo inicial y final de fraguado. En los casos del 50% y 75% de escoria en el sistema, el tiempo inicial de fraguado se reduce drásticamente, lo mismo que el tiempo final de fraguado. La Calorimetría (Figura 1. der.) muestra que la hidratación del cemento portland está controlada por los silicatos e inicialmente por la reacción entre el aluminato de calcio y el yeso. Al momento de incorporar escoria blanca, la hidratación inicial de los aluminatos se incrementa (pico en las primeras horas) y la hidratación de los silicatos se desplaza.



Figura 1: Tiempos de fraguado (izq.) y calorimetría semi-adiabatica (der.) de las pastas con escoria blanca

La evolución de la resistencia a compresión de los morteros con diferentes remplazos de cemento se puede observar en la Figura 2 (izq.). El mortero control es el que mayor resistencia obtiene desde fabricación hasta los 7 días, mientras la ganancia de resistencia es menor de 28 a 90 días. A medida que se incorpora escoria blanca la resistencia disminuye significativamente, y se hace crítica en contenidos de escoria de 75% pues a 7 días la resistencia es de solo 1 MPa. Esta situación está de acuerdo a los resultados de calorimetría, los cuales muestran un retardo significativo de la hidratación de los silicatos de calcio.





Figura 2: Resistencia a compresión (izq.) y expansión en cámara húmeda (der.).

En cuanto a la inestabilidad volumétrica (Figura 2 (der.)) se puede ver que las expansiones en todos los casos son similares a las del mortero control. No obstante, en el caso del 75% de escoria parece que a 160 días presenta un ligero aumento de la expansión, lo cual podría ser debido a la hidratación lenta de la periclasa.

4. Conclusiones

Basados en los resultados experimentales, las conclusiones de este trabajo se pueden resumir en los siguientes puntos:

- La incorporación de escoria blanca en cantidades del 50 y 75% genera una merma en los tiempos iniciales y finales de fraguado, generando problemas de trabajabilidad. También se observa que la presencia de aluminatos de calcio de la escoria blanca genera una reacción inicial más rápida del material y la composición de la escoria genera un retardo en la hidratación de los silicatos de calcio del cemento.
- La incorporación de escoria blanca genera una reducción de resistencia proporcional a la cantidad de escoria en el sistema. Sin embargo, es posible obtener morteros de 30 MPa o 45 MPa a los 28 días. Hasta los 200 días no se observan procesos expansivos preocupantes en los morteros.

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ESTUDIO EXPERIMENTAL SOBRE LA PENERACIÓN DE IONES CLORURO EN HORMIGONES CON ÁRIDOS RECICLADOS

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Resumen

Como se sabe la degradación de estructuras de hormigón armado debido a la penetración de cloruros tiene una influencia significativa en la durabilidad. En este trabajo, se realiza una campaña experimental para determinar el efecto del árido reciclado y el método de dosificación del hormigón en la resistencia a la penetración de iones cloruro en los hormigones con áridos reciclados. Los métodos de diseño utilizados son el ACI, remplazo del 20% en volumen de árido natural por áridos reciclados (basado en la ACI) y, finalmente, el método de volumen de mortero equivalente (EVM). Los resultados de penetración de cloruros indican que el hormigón con áridos reciclados (ACI) muestra los mayores valores de difusión, mientras el hormigón diseñado con el EVM presenta valores de difusión similares a los del hormigón convencional.

1. Introducción

Debido al continuado aumento de la industria de la construcción, las cantidades de residuos de construcción y demolición generados en Europa y España continúan incrementando cada año [1]. Uno de los principales inconvenientes que se ha presentado con la utilización de áridos reciclados es que presentan diferencias con los áridos naturales en cuanto a porosidad, absorción de agua, fisuración siendo mayores en los primeros y que tienen una influencia importante en la durabilidad de las estructuras de hormigón. Igualmente, los áridos reciclados se pueden entender como un material con dos fases siendo una de ellas el "mortero adherido" y, la otra, el "árido natural" al que está adherido dicho mortero.

Generalmente, para fabricar hormigones con áridos reciclados se han utilizado métodos convencionales de dosificación como el de Fuller, Bolomey o el ACI. Sin embargo, para obtener comportamientos similares a los hormigones con áridos naturales, en términos de resistencia y porosidad, se utilizan mayores cantidades de cemento. Con la finalidad de resolver este problema, Fathifazl [2] ha desarrollado un método de dosificación para poder utilizar el máximo de áridos reciclados, denominado "método de volumen de mortero equivalente" o EVM por sus siglas en ingles. Este método reduce la cantidad de cemento en el hormigón ya que considera al mortero adherido en los áridos reciclados como parte del contenido total de mortero requerido en el hormigón.

Debido a que este método de dosificación ha sido propuesto recientemente, resulta importante estudiar la durabilidad de los hormigones fabricados bajo dicha metodología. En este sentido, el objetivo de este



determina la influencia de la cantidad de árido reciclado y del método de dosificación en la penetración de iones cloruros en hormigones con áridos reciclados.

2. Materiales y metodología

En este trabajo se utiliza cemento portland CEM I 52,5R, árido fino y grueso natural (0/5mm y 4/16 mm), de origen calizo, con densidades y absorciones de 2,66 kg/m3 y 1,1% y 2,69 y 0.5% respectivamente. Se utiliza un árido grueso reciclado de hormigón (4/16 mm) con una densidad de 2,43 kg/m3 y una absorción de 6,3%. El contenido de mortero árido en el árido reciclado es del 35%. Igualmente se utiliza un aditivo superplastificante MasterGlenium Sky 604.

Se evalúan tres tipos de hormigón, a saber:

- Bconv/0.4-1: Hormigón control, fabricado con áridos naturales finos y gruesos, diseñado bajo la metodología Bolomey. Relación a/c de 0,4 y un contenido de aditivo superplastificante del 1%.
- Bdvr20/0.4-1: Hormigón con 20% de remplazo de árido natural por reciclado, en volumen.
 Diseñado bajo la metodología Bolomey. Relación a/c de 0,4 y un contenido de aditivo superplastificante del 1%.
- Bemv20/0.4-1.7: hormigón con un 20% de remplazo de árido natural por reciclado. Diseñado bajo la metodología del "volumen de mortero equivalente EMV". Relación a/c de 0,4 y un contenido de aditivo superplastificante de 1,7%.

Las dosificaciones estudiadas se muestran en la Tabla 1.

Hormigón	Agua (kg)	Cemento (kg)	Árido natural fino (kg)	Árido natural grueso (kg)	Árido reciclado grueso (kg)	SP (kg)
B _{CON} /0.4-1	182	455	835	1031	-	4.6
B _{DVR} 20/0.4-1	182	455	835	794	203	4.6
B _{EMV} 20/0.4-1.7	169	422	774	887	227	7.2

Tabla 1: Dosificación de los diferentes tipos de hormigones estudiados

Se determina la resistencia a compresión (UNE EN 12390-3. 2020) y la absorción (ASTM C642. 1997) de los tres tipos de hormigones a la edad de 28 días. La penetración de iones cloruros se determina según la norma NT Build 443 [3], utilizando especímenes cilíndricos de hormigón de 10 cm de diámetro y 5 cm de altura de cada tipo de hormigón, a la edad de 28 días. Las muestras se introducen en una solución de 165 g de NaCl por litro y se dejan por un periodo de 35 días. Seguido se extraen y obtienen ocho capas desde la cara en contacto con la solución hacia el interior de las muestras, determinando el contenido total de cloruros en cada capa. Finalmente, se determina el coeficiente de difusión utilizando la segunda ley de Fick.



3. Resultados y discusión

Los resultados de resistencia a compresión (Figura 1a) muestran que el valor medio de los tres tipos de hormigones es de 60 MPa. En el caso del hormigón con remplazo directo (Bdvr) el valor es de 58 MPa ligeramente inferior, pero se puede observar que la variación es ligeramente mayor. El hormigón control y el hormigón Bemv20 presentan igual resistencia compresión al tener igual volumen de mortero (fresco y adherido). Sin embargo, el hormigón Bdvr20 presenta mayor contenido de mortero, lo que genera una merma en la resistencia.



Figura 1: a) Resistencia a compresión y b) absorción de los diferentes tipos de hormigón

La absorción de los tres tipos de hormigones está en el rango de 4,3% hasta 5,3%, siendo el hormigón con remplazo directo el que tiene el mayor valor de absorción (5,1%).

En relación a la penetración de iones cloruro, se observa que la concentración en superficie de cloruros para el hormigón con remplazo directo (Bdvr20) es la más alta, alcanzando un valor de 0.9%. El hormigón diseñado por el método EMV presenta valores ligeramente superiores a 0,75%, mientras el hormigón control presenta valores de 0,68%. A partir de los datos de concentración en superficie, se determina el coeficiente de difusión y se modelan los resultados experimentales, mostrados en la Figura 2.





Figura 2: Perfiles de penetración de cloruros para los tres tipos de hormigones y sus respectivas curvas modeladas con la segunda ley de Fick (ensayos a 35 días de inmersión)

En la Figura 2 también se observa que el hormigón Bdvr20 presenta un mayor decrecimiento en la concentración de cloruros con el aumento de la profundidad en relación a los otros dos tipos de hormigones, los cuales presentan un comportamiento similar.

Una de las posibles causas de que el hormigón Bdvr20 presente un mayor decrecimiento de la concentración de cloruros entre capa y capa es la capacidad de fijación que tiene este hormigón. Este comportamiento ya fue mencionado por Beaudoint et, al. [4], el cual plantea que la cantidad de cloruros fijados es directamente proporcional a la cantidad de gel CSH. Finalmente, en la Tabla 2 se muestran los resultados del coeficiente de difusión de cloruros, obtenidos a partir de la segunda ley de Fick. El coeficiente de difusión está influenciado por parámetros como porosidad e interconexión de poros, por lo cual, se puede tener un mayor coeficiente de difusión y una alta capacidad de fijación de cloruros.

Hormigón	Tiempo (días)	Cs para Cl- totales (%)	De para Cl- totales (m2/s)
B _{CON} /0.4-1	35	0.676	1.89E-11
B _{DVR} 20/0.4-1	35	0.915	1.93E-11
B _{EMV} 20/0.4-1.7	35	0.756	1.43E-11

Tabla 2: Parámetros de concentración superficial y coeficiente de difusión para los hormigones

Como se observa, el hormigón Bemv20 presenta el coeficiente de difusión más bajo, seguido del hormigón convencional y, finalmente, el hormigón con remplazo directo (Bdvr20).



4. Conclusiones

Basados en los resultados experimentales, las conclusiones de este trabajo se pueden resumir en los siguientes puntos:

- La resistencia a compresión es similar en los tres tipos de hormigones estudiados, obteniéndose valores de 60 MPa.
- El hormigón diseñado por el método de mortero equivalente presenta un coeficiente de difusión a cloruros menor que el hormigón control y, éste menor que el hormigón con remplazo directo.
- Es posible que la incorporación de áridos reciclados ayude en la fijación de cloruros, pero es un tema que se debe estudiar en mayor profundidad.

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DESIGN OF 3D PRINTING CONCRETE WITH SUSTAINABLE MATERIALS

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Abstract

One of the most important issues to get an optimal 3D printing concrete is the suitable mix design and the specific requirements in terms of extrudability and buildability. This research proposes different concrete mixes with fly ash, metakaolin, limestone filler and aluminium sulphate to obtain a concrete dosage that fulfils printability requirements in terms of buildability. This is evaluated through open time and shape retention tests at different ages (15, 40, 60 and 80 min). Based on these results an optimal mix is selected to evaluate mechanical strengths under different loading directions to simulate the influence of printing process and the performance of concrete interlayer. Finally, it can be concluded that the use of 1% of aluminium sulphate might be a suitable concrete dosage for 3D printing applications.

1. Introduction

During the last decades, different raw materials have been used replacing aggregates or clinker that have allowed conventional concrete to improve its properties and advance in the field of sustainability. In this line, different studies have focused on increasing the concrete durability and better construction processes [1,2].

Digital concrete shows numerous benefits, diminishes the material consumption and therefore encourages sustainability, offers higher productivity and faster construction procedures, minimizes human resources, reduces material wastes, presents higher cost efficiency ratio and promotes the efficient use of natural resources.

The main objective of this research is to design a sustainable 3D printing concrete that fulfil the requirements in terms of printability, mechanical response and durability for real applications using supplementary cementitious materials, fibres and porous aggregates from waste materials as water reservoirs for internal curing. The use of these aggregates improves the bond between layers and control the autogenous shrinkage, especially at early ages. The extrusion will be the printing system to obtain the 3D concrete analysed in this research.

This paper focus on a first stage where conventional concrete is designed to fulfil the printability requirements. To do that, a self-compacting concrete is designed using ordinary Portland cement, metakaolin, fly ash and limestone filler. In addition, aluminium sulphate was incorporated to improve printability properties of concrete at early ages.



2. Materials and mixes

2.1 Cements and supplementary cementitious materials

In this study, Ordinary Portland Cement (OPC) CEM-I 52,5, fly ash (FA), metakaolin (MK) and limestone filler (LF) have been used. These materials have a BET specific surface of $1,36 \text{ m}^2/\text{g}$, $3,33 \text{ m}^2/\text{g}$, $4,25 \text{ m}^2/\text{g}$ and $1,44 \text{ m}^2/\text{g}$, respectively. In addition, to guarantee the extrudability and buildability of concrete, specific additives will be required. A high range water reducing admixture was used, masterEase 3850, to guarantee suitable rheological properties for printing concrete, and aluminium sulphate (AS) to control the hydration development, to shorten the setting time and to improve concrete properties at early ages required for printing concrete. Different percentages of this additive have been assessed: 0,5%, 0,8% and 1%. Finally, 1% of AS was considered as optimal content.

2.2 Aggregates

In this research, conventional crushed sand has been used with a maximum particle size of 4 mm, fineness modulus of 2.78, water absorption of 2.43% and density of 2.47 kg/m³. As alternative aggregates, in following stages fine aggregates from biomass of wood industry will be used. These aggregates present a similar fineness modulus (2.74) to conventional sand and maximum size of 4 mm, however, water absorption is significant higher (36%) and density lower than that of sand (1.14 kg/m³). This material will be used as water reservoir for internal curing to improve the 3D printing concrete performance.

2.2 Concrete dosages

Based on literature review and previous works, key parameters have been defined to obtain a concrete dosage [3]. At this first stage, SCC with conventional sand is designed to obtain suitable performance in terms of printability for 3D printing applications. First, a conventional concrete (M1) with OPC, MK and FA was analysed. This mix did not present suitable performance for printing applications so, LF was included instead of FA. This was the baseline of serie2 (M2-0). Finally, to improve printability properties of concrete 1% of AS was incorporated as additive (M2-1). The Table 1 lists concrete dosages.

Table 1: Concrete dosages

		Cement	FA	МК	LF	Water	AS	Conventional sand
Serie1	M1	439,64	311,41	179,66		422,73		600,75
Serie2	M2-0	339,36		277,36	143,58	266,49		1111,50
	M2-1	339,36		277,36	143,58	266,49	7,60	1111,50



3. Experimental program

The use of supplementary cementitious materials modifies concrete properties in terms of buildability and extrudability. So, different concretes have been analysed to determine if they fulfil the printability requirements. Tests to determine the shape retention and open time for mixes were performed. In addition, mechanical strengths were obtained only for the optimal mix selected in the series 2.

3.1 Open time test

Open time tests were performed according to EN 1015-9 at different ages (15, 40, 60 and 80 minutes) using a penetrometer device. This test was carried out after 10 minutes of rest and immediately after casting to obtain a static and dynamic analysis, respectively.

3.2 Shape retention

Shape retention was determined using cylindric specimens of 75 mm of diameter and 50 mm of height. To analyse this property over time, shape retention was measured at 15, 40, 60 and 80 min. Concrete specimens were casted at 10 minutes and then, they were kept at rest up to 15, 40, 60 and 80 min, when this property was measured. The evolution over time of shape retention also provides information regarding the effect of thixotropy.

3.3 Mechanical strength

Prismatic specimens of 4x4x16 cm were used to measure compressive and flexural strength according to EN 196-1 at 48 hours. Three specimens were casted in one layer and they were used as reference (15/15, conventional casting). The other specimens were casted in two layers simulating the printing process. The first layer was casted at 15 min and the second one at 40 min (15/40), at 60 min (15/60) and at 80 min (15/80). To evaluate the effect of printing process different loading directions, perpendicular (perp.) and parallel (paral.) to casting layers (Figure 1) were applied to obtain the compressive strength and flexural strength of conventional casting specimens and printed ones. Other properties are being evaluated as shrinkage at early ages and green strength through digital image correlation (DIC), Figure 2.





Figure 1. Loading directions for mech. strength tests

Figure 2. Green strength test through DIC



4. Results and Discussion

Figure 3 shows the results obtained for penetration resistance of different mixes. As can be seen, this resistance increases with time, especially for static analysis, M2-1-15min after 40 minutes and when AS is used. The penetration resistance is directly related to buildability of concrete, especially the static analysis that simulates the printing process placing concrete layers after a period of time. These results reveal that the use of AS contributes to enhance the buildability of concrete and therefore, it will be necessary to design a 3D printing concrete.

Another import property is the shape retention of mixes. Figure 4 shows the shape retention factor at different ages for concrete mixes. These values were calculated as the relationship between the diameter of specimens before demoulding and after demoulding. Again, concrete with AS presents a better performance than M1 (without AS) in terms of shape retention.

Based on these results, concrete with 1% of AS of cement content (M2-1) is considered as the optimal mix to continue with further analysis. In this line, mechanical strengths were determined at 24 hours.

Table 2 lists compressive strength and flexural strength of the optimal concrete mix considering specimens made using conventional casting and those casted in two layers at different ages (at 15 min the first layer and at 40, 60 and 80 min the second one). These results reveal a slight reduction of mechanical strengths when specimens are casted in two layers.



Figure 3. Open time at different ages



Figure 4. Shape retention tests at different ages

		-			
(MPa)	Conventional casting	15 /40 min	15/60 min	15/80 min	-
Flexural strength perp.	6,32	6,00	6,16	6,28	-
Flexural strength paral.	6,39	6,22	6,15	6,09	
Compressive strength perp.	20,58	19,71	18,34	14,59	
Compressive strength paral.	22,80	22,70	22,67	22,62	

Table 2: Mechanical strengths of M2-1



5. Conclusions

The use of AS contributes to enhance the buildability of concrete and does not present detrimental effects in terms of mechanical strengths when concrete specimens are casted in two different layers. Therefore, concrete dosage M2-1 might be used as baseline for future steps of this research. Anyway, more properties need to be analysed to guarantee this concrete fulfil all printability requirements. Further research is being also developed to incorporate fibres and porous aggregates from waste materials as water reservoirs for internal curing.

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ALKALI ACTIVATED CEMENTS BASED ON COPPER SLAG AND REINFORCEMENT WITH OLIVE PRUNING FIBERS

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Abstract

In recent decades, it has appeared a lot of research to replace traditional Portland cement, in order to reduce the environment impact. Alkali activated cement is the material that the best results has obtained. Although they present flexural problems. For this reason, it has grown the interest in reinforcing these materials by adding fibres. In this work, a comparative study has been carried out using fibre from olive tree pruning as reinforcement. Fibres were subjected to different treatments to improve mechanical properties. Three different solutions were used: 10 wt. % Na₂SiO₃, 3 wt. % CaCl₂ and 5 wt. % NaOH. Copper slag was used, obtained in the refining operation of copper extraction, as a precursor material in the manufacture of alkali activated cement. A solution of 35 wt. % KOH (12M) and 65 wt. %K₂SiO₃ was used as activator. The results showed that olive pruning fibres could be used as reinforcement, with the optimal amount of fibres, being 0.5 wt. % for this precursor material.

1. Introduction

Alkali activated materials have been extensively studied, demonstrating that it is possible to produce a green cement from different sources of natural minerals or wastes [1]. In recent years, research has appeared using fibres as reinforcement to improve mechanical properties. Studies have shown that adding fibres to the matrix increases the flexural strength of composites [2].

Among the raw materials used to form green cements are industrial by-products, such as metallurgical slag, fly or bottom biomass ash, or natural minerals, such as clays. Slags have been widely studied, due to their composition.

Fibres can be synthetic or natural. Synthetic fibres are commercially produced and they have been used in other compounds. Due to the growing interest in creating more environmentally friendly materials, fibres of natural origin are being studied [3]. Natural fibres can be classified as woody or non-woody fibres [4], depending on their composition and origin. These fibres can be used untreated or treated. Treatments can be physical or chemical. There are several treatments to develop on natural fibres: hornification: wet and dry cycles [5]; mercerization: immersion of fibres in a solution (NaOH) [6, 7]; silane treatment: immersion



of fibres in a silane solution [8-10]; a combination between them [9, 11]; or other treatments [12]. They are some of treatments developed in the available literature.

In this study, copper slag (CS) has been used as a precursor. This slag is a by-product of the metallurgical industry in obtaining copper from scrap. Specifically, this slag is made up of iron silicate, a by-product used as an abrasive and as an aggregate in the construction of bases and sub-bases of highway esplanades. This research analyses the effect of fibres in the binder matrix. The aim is to improve the flexural strength properties. Thus, the olive fibres were treated with different solutions: 10 wt. % Na₂SiO₃, 3 wt. % CaCl₂ and 5 wt. % NaOH. Results show clear differences between treatments, demonstrating the possibility of use fibres as reinforcement in alkali activated cements.

2. Materials and methods

2.1 Raw materials

Copper slag used as precursor was supplied by Atlantic Copper company, located in Huelva (Spain). This raw material was ground in a ball mill to a particle size of less than 0.1 mm. Chemical composition of precursor was obtained by X-ray fluorescence (XRF), and is shown in Table 1. These XRF results show that the main component of the copper slag is Fe_2O_3 (62.18 %) and SiO_2 (27.65 %), with small amounts of Al_2O_3 (2.04 %) and CaO (1.25 %).

Table 1: Chemical composition of raw materials.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	K2O	MgO	MnO	SO ₃	P2O5	LOI
CS	27.65	2.04	62.18	0.63	1.25	0.56	0.38	0.03	0.90	0.04	0.00

As alkaline activator, a solution mixing 35 wt. % of KOH (12M) and 65 wt. % of potassium silicate (K_2SiO_3) was used. This activator was fixed according with results of previous works [13]. KOH was provided by GlobalChem (85% purity) and K_2SiO_3 by Roth (composition: 7.5-8.7 wt. % K_2O , 19.5-21.8 wt. % SiO₂ and 69.5-73 wt. % H₂O). Thus, the Ms modulus (SiO₂/K₂O) of the activator obtained was 1.38 and the liquid/mixture ratio used was 0.35 for all composites. Whole solution is considered as liquid (water + solid reactive), and mixture are precursors and fibres.

The fibres used as reinforcement were obtained from olive tree pruning. They were crushed until obtaining the retained range between 0.125 and 0.250 mm. Three treatments were developed to improve mechanical properties of composites. The treatments consisted of immersing fibres in a solution for 60 minutes with agitation. Subsequently, they were drained, dried in an oven, and stored sealed until the manufacture of composites. Solutions used as fibre treatment were: 10 wt. % Na₂SiO₃, 5 wt. % NaOH and 3 wt. % CaCl₂. Different proportions were used to reinforce the cement matrix: 0.25 wt. %, 0.5 wt. %, 0.75 wt. %, 1 wt. %, 3 wt. % and 5 wt. %. Composites manufactured were designated according to the fibre treatment used:



UT, untreated fibre; S, sodium silicate treatment; M, mercerization (NaOH); and C, $CaCl_2$ treatment; followed by the fibre percentage used. The control paste was designated as Control.

All the pastes were manufactured following the same sequence. The precursor and fibres were mixed in a planetary mixer for 90 seconds, and subsequently the activator solution was poured, mixing all materials for 90 seconds in the planetary mixer. After this process, the fresh paste was poured into prismatic steel moulds (60x10x10 mm). Moulds with fresh paste were subjected to ultrasound for 60 seconds, in order to eliminate bubbles caused during the pouring and spreading of the material into moulds. Filled moulds were stored in a climatic chamber at 20 °C and 90% humidity, for 24 hours. After this time, they were removed from the mould and they were placed back in the climatic chamber under same conditions, until test day.

Mechanical properties (flexural and compressive strength) were obtained at 7 and 28 days of curing, following UNE-EN 1015–11:2000/A1:2007 standard [14].

Table 2:	Code	for	different	composites	manufactured.
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Code	Control	UT	S	Μ	С
Treatment	Control	Untreatment	10 % Na ₂ SiO ₃	Mercerization (5 % NaOH)	3 % CaCl ₂

3. Results and Discussion

The effect of olive pruning fibre as reinforcement in flexural strength of alkali activated cement with different percentages and curing time is shown in the Figure 1. The best value was obtained using a percentage of 0.5 wt. % of fibres treated with a $CaCl_2$ solution (8.0 MPa) after 28 days of curing. This percentage of addition is consistent with other studies [3]. Comparing control paste (5.9 MPa) with composites reinforced, a significant improvement in flexural strength is observed.

Fibres treated with sodium silicate also produced an increase in flexural strength with the same percentage of fibre addition (6.9 MPa), although to untreated fibres with the same percentage of addition (7.0 MPa). On the other hand, fibres treated with NaOH needed a higher optimal percentage, increasing up to 0.75 wt. % (6.3 MPa), also achieving higher strength than control paste. More than 1 wt. % fibre addition did not produce an increase in flexural strength respect to reference paste. These results are consistent with available literature, where the optimal amount of fibre reinforcement varies between 0.5 and 3 wt. % [3, 15, 16].





Figure 1: Flexural strength with different fibre percentage addition and curing time.

Compressive strength results of alkali activated cements reinforcement with olive pruning fibres are shown in the Figure 2. Composites reinforced with fibres obtained lower compressive strength values than control paste. Compressive strength values decrease as the amount of fibres added increases. This behaviour is contrary to other studies, which achieved an increase in compressive strength, due to the good dispersion of the fibres in the matrix, helping to increase the matrix-fibre interaction [15]. However, the loss of resistance could be considered acceptable, due to the high compression values obtained. Adding a percentage of up to 0.75 wt. %, all composites obtain strengths above to 30 MPa.



Figure 2: Compressive strength with different fibre percentage addition and curing time.

Conclusions 4.

The effect of olive pruning fibres as a reinforcement has been demonstrated. The optimum percentage for this reinforcement was 0.5 wt. % in terms of flexural strength. The treatment that gives rise to the best fibre-matrix compatibility is the use of a solution of 3 wt. % of CaCl₂, improving values of the control paste. The fibres treated with 10 wt. % of Na₂SiO₃ or untreated fibres also obtained good flexural strength values, higher than those of the control paste. As a consequence of this fibre addition, the compressive strength decreased with increasing fibre content. Although the decrease was considered admissible for percentages up to 0.75 wt. %.



The results indicate that fibres can be used as reinforcement of binders made from copper slag, varying their behaviour according to the treatment and the percentage of added fibre.

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BLAST FURNACE SLAG REPLACED BY BIOMASS BOTTOM ASH IN THE MANUFACTURE OF ALKALI ACTIVATED CEMENTS

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Abstract

The use of biomass bottom ash replacing blast furnace slag as precursor was studied in this work. Besides silica fume was added as extra silica in the manufacture of alkali activated cements. A potassium hydroxide KOH (8M) solution was used as activator. Pastes synthetized were characterized by compressive strength test at 1, 7 and 28 days of curing. Data show the possibility of improve mechanical strength replacing blast furnace slag by biomass bottom ash, although strength could be lower than control paste at early ages.

1. Introduction

Ordinary Portland cement (OPC) is the most widely used construction material, but its manufacture carries serious environmental risks. The reason is the high consumption of natural resources and the emission of greenhouse gases [1]. In order to reduce its impact, a multitude of research have been carried out with the aim of substituting or replacing traditional Portland cement. Alkaline activated materials are materials that have managed to reduce their impact on the environment due to the possibility of using waste as raw material [2]. These alkali activated materials require a precursor and an activator [3].

As precursors, materials rich in aluminosilicates are necessary, and in the case of the activator, commercial solutions such as alkaline hydroxides and alkaline silicates have normally been used [4]. The main benefit of these materials is the use of waste and industrial by-products, thus reducing their deposit in landfills and avoiding emissions in their production. Blast furnace slags (BFS) are materials that have been extensively studied, as well as the addition of silica fume [5]. But there is not yet an extensive bibliography of studies using bottom ash in the production of alkali-activated cements.



This work aims to improve properties of slag-based alkali activated cements, by replacing them with ashes, and adding silica fume as an extra silica supply. For this, a KOH (8M) solution was used as activator. The manufactured pastes were tested for compressive strength at 1, 7 and 28 days of curing. Results showed that the substitution of BFS by biomass bottom ash (BBA) improved the properties of alkali activated cements, being 25 wt. % the optimal percentage.

2. Materials and methods

2.1 Raw materials

Blast furnace slag (BFS), biomass bottom ash (BBA) and silica fume (SF) were used as precursors in the manufacture of alkali activated cements. Blast furnace slag is from cement plant located in Carboneras (Almería, Spain), biomass bottom ash is produced in a biomass power plant sited in Mérida (Spain) as a waste from eucalyptus and other biomass combustion. Silica fume was supplied by FerroAtlántica. Raw materials were crushed to a particle size of less than 0.125 mm. Alkaline activator used was a KOH 8M solution. A GlobalChem KOH commercial at 85% of purity was used. Chemical compositions of raw materials is shown in Table 1.

BFS is mainly composed of CaO (52.68 wt. %) and SiO₂ (26.19 wt. %), and significantly content of Al_2O_3 (9.23 wt. %). In the case of BBA, it formed mainly of SiO₂ (55.72 wt. %) and it has high content of CaO (14.99 wt. %), Al_2O_3 (10.58 wt. %) and K_2O (7.93 wt. %). Silica fume is fundamentally formed of SiO₂ (94.14 wt. %).

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	Fe ₂ O ₃	MgO	MnO	SO ₃	P_2O_5	LOI
BFS	26.19	9.23	0.69	0.79	52.68	0.46	6.90	0.20	1.38	0.01	0.00
BBA	55.72	10.58	7.93	0.98	14.99	4.88	2.56	0.19	0.43	0.70	3.31
SF	94.14	1.19	1.35	0.00	1.97	0	0	0.11	0.49	0.23	0.00

Table 1: Chemical composition of raw materials (wt. %).

2.2 Mix proportions

Six different binder were carried out mixing blast furnace slag and biomass bottom ash (25-50 wt. %), with addition of silica fume (5-10 wt. %). Mix proportions is shown in the Table 2. All binders were manufactured using the same liquid/binder ratio of 0.5.

Precursors (BFS, BBA and SF) were mixed in a planetary mixer for 30 seconds. Subsequently, the KOH (8M) solution was added to the mixer and materials were homogenised for 60 seconds. Fresh pastes were poured in silicon moulds 15x15x10 mm. Pastes were cured at ambient temperature in the laboratory until test day.



	BFS (wt. %)	BBA (wt. %)	SF added (wt. %)
100BFS	100	-	0
25BBA-0SF			0
25BBA-5SF	75	25	5
25BBA-10SF			10
50BBA-0SF			0
50BBA-5SF	50	50	5
50BBA-10SF			10

Table 2: Binder mix proportions.

2.3 Compressive strength

All binders were tested by compressive strength at different curing time: 1, 7 and 28 days, according with the standard UNE-EN 196-1:2018 [6]. A Ibertest Electrotest-300-MD2 machine was used to carry out the test. Force speed used was 50 N/s and three samples were tested for each age of curing.

3. Results and Discussion

Compressive strength results are shown in the Figure 1. Results show that at early ages, 1 day, the compressive strength is greater in the control cements and samples with the incorporation of 25 wt. % of BBA. While at 7 days, samples with 25 wt. % replacement increase their resistance above the control sample (23.8 MPa), obtaining strengths between 25 and 28 MPa. The incorporation of 25 wt. % SF has a positive effect in mechanical properties, however addition above 10 wt. % has a less effect.

Compressive strengths obtained can be considered sufficient for structural use, although results are significantly lower than other studies, which achieved strengths above 30MPa after 7 days of curing. [7]. Angulo-Ramirez et al. used BFS with 20 wt. % OPC replacement and a NaOH solution as activator, obtaining slightly lower values than the present study [8]. Although the data improved when using waterglass. In other studies, using higher percentages of SF, compressive strength values were lower [9]. Comparing data at 28 days of curing, binders manufactured with BBA and SF improved these values, although the best result was obtained for control paste. SF improved compressive strength in binders with 25 wt. % BBA when the optimal SF percentage was used [10].





Figure 1: Compressive strength at different curing time.

4. Conclusions

Results show that a replace with 25 wt. % ash improves the compressive strength. With 50 wt. % substitution improvements are also obtained, but these are shown in the long curing time. The addition of 5 wt. % SF achieve to improve results at longer curing times.

Data obtained demonstrated that pastes manufactured with BFS and BBA could use as cementitious material and they could improve with SF addition.

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USE OF SEAWATER IN RECYCLED AGGREGATE CONCRETE

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Abstract

This research intends to analyse the feasibility of using seawater in concrete, both in the composition and in curing, in detriment of potable water. It also intends to evaluate the behaviour of concrete produced with different replacement ratios of coarse natural aggregates (NA) with coarse recycled aggregates (RA) (0%, 50% and 100%). The mechanical characterization of the mixes was carried out through the tests of compressive strength, splitting tensile strength, modulus of elasticity and abrasion resistance. In most mechanical tests, the simultaneous use of RA and seawater, both in the composition and curing, causes significant losses in performance. To evaluate the mixes in terms of durability, tests of water absorption by immersion and capillarity, resistance to carbonation and chloride penetration, and shrinkage were performed. It was found that the use of seawater in the composition worsened the performance of concrete produced with and without RA. Regarding the performance of seawater curing, it was found that it worsened the behaviour of concrete in terms of water absorption.

1. Introduction

According to the National Water Council, Earth is made up of 70% water, and only 7% of that is potable. Thus, potable water is one of Earth's most precious resources and, in view of its high consumption, it is a great challenge to learn how to save it due to its scarcity in many parts of the world.

The accumulation of construction and demolition waste (CDW) in landfills also causes major environmental concerns. Thus, the use of coarse recycled aggregates (RA), as an alternative to coarse natural aggregates (NA), allows mitigating energy consumption and environmental pollution.

Concrete is the most widely used construction material worldwide and is accompanied by huge carbon emissions and negative impacts on the environment. In this context, to reduce energy consumption and save natural resources, obtaining a "greener" concrete, the use of seawater and coarse aggregates becomes a promising option, also allowing a relief in the resource crisis.

Nowadays, the use of seawater in reinforced concrete structures is inadvisable, unlike in non-structural concrete [1]. Seawater can be incorporated into various unreinforced concrete elements, including concrete blocks, floors or lightweight concrete. In recent years, reinforcement not subject to corrosion has been developed, such as carbon fibres, glass fibres, stainless steel and reinforcement coated with epoxy resin [2]. This provides an attractive solution that can replace the use of steel as a reinforcement material and solve durability problems in reinforced concrete structures containing seawater.



2. Materials and testing methodologies

2.1 Cements

In the present experimental campaign, seven materials were used to produce concrete: cement type I 42.5R (300 kg/m³ of concrete); seawater; potable water; coarse recycled aggregates; river sand, natural limestone; superplasticizer (SP) SikaPlast-717 (1% of cement).

2.2 Composition of concrete

In this research, 12 concrete mixes were produced. The aim is that the mixes produced have a composition as identical as possible to that of the reference concrete (RC). Table 1 shows the water/binder ratios of all the mixes. It was necessary to add extra water to the mixes with seawater and/or RA. However, regarding the use of RA, the effective w/c ratio was maintained. The mixes with seawater required a higher effective w/c ratio. This is attributed to the presence of large amounts of sodium chlorides contained in seawater, which accelerate the hydration of cement.

Mixes	CRA	Effective water/binder ratio	Total water/binder ratio
P-CP-0 (RC)	0		0.55
P-CP-50	50	0.55	0.59
P-CP-100	100		0.63
S-CP-0	0		0.58
S-CP-50	50	0.58	0.62
S-CP-100	100		0.66
P-CS-0	0		0.55
P-CS-50	50	0.55	0.59
P-CS-100	100		0.63
S-CS-0	0		0.58
S-CS-50	50	0.58	0.62
S-CS-100	100		0.66

Table 1: Water/binder ratios of the concrete mixes

2.3 Tests

The characterization of the mixes in the hardened state was carried out through the following tests: compressive strength tests were made on 15 cm standard cube specimens, according to NP EN 12390-3 (three cubes were tested at 28 days); splitting tensile strength tests followed NP EN 12390-6 and were made on cylinders with diameter of 150 mm and height of 300 mm (two cylinders were tested at 28 days); two cylinders (diameter of 150 mm; height of 300 mm) were tested for Young's modulus at 28 days as specified in LNEC E 397; abrasion resistance tests were made on 10 cm cube specimens according to DIN 52108 (two cubes were tested at 91 days); water absorption by immersion tests followed LNEC E394 (three cubes were tested at 28 days); water absorption by capillarity tests were made as specified in LNEC E393 (two



cylinders were tested at 28 days); carbonation resistance tests were made according to LNEC E391 (three cylinders were tested at 28 days); chloride ions penetration resistance tests followed LNEC E463 (three cylinders were tested at 28 days); shrinkage at 91 days was analysed according to LNEC E398.

3. Results and discussion

3.1 Fresh-state properties

In the fresh state, the mixes were analysed through the Abrams cone test and density. The purpose of this test was to ensure a constant workability in all mixes (slumps in the range of 100 to 150 mm - S3). The replacement of NA with RA reduces the density both in mixes with seawater and potable water, due to lower density of RA (density between 2173 kg/m³ and 2335 kg/m³).

3.2 Hardened state properties

The results obtained in the mechanical tests are summarized in Table 2, in terms of the variations relative to RC. The table also shows the results obtained in the tests carried out on the RC.

Mix	Compressive	Splitting tensile	Modulus of	Abrasion resistance
	strength at 28 days	strength at 28 days	elasticity at 28 days	at 91 days
P-CP-0 (RC)	- (44.3 MPa)	- (3.7 MPa)	- (40.7 GPa)	- (4.6%)
P-CP-50	-9%	-29%	-23%	9%
P-CP-100	-33%	-40%	-36%	22%
P-CS-0	-3%	-7%	-1%	-15%
P-CS-50	-11%	-34%	-21%	9%
P-CS-100	-34%	-52%	-39%	17%
S-CP-0	-4%	-22%	-4%	7%
S-CP-50	-10%	-30%	-24%	8%
S-CP-100	-26%	-46%	-40%	17%
S-CS-0	-6%	-27%	-5%	6%
S-CS-50	-12%	-38%	-24%	5%
S-CS-100	-34%	-41%	-42%	11%

Table 2: Results of the mechanical tests

The compressive strength showed that the RC belongs to strength class C30/35. With the incorporation of seawater and RA, the compressive strength of the mixes was affected. This is due to an increase in the replacement ratio of NA with RA, as well as the higher w/c ratio of all mixes with seawater. On the other hand, it may also be due to the formation of gypsum, which causes expansive crystallization pressure.

There was also a reduction of the splitting tensile strength with the use of RA and seawater, due to the increase of the w/c ratio of the mixes. The incorporation of seawater in the composition drastically reduced the splitting tensile strength, leading to a decrease of approximately 20%, compared to the RC.



It was also concluded that there was a decrease in the modulus of elasticity of the mixes with the replacement of NA with RA and the use of seawater. Mix S-CS-100 was the one that showed the worst result (decrease of 42%).

It was found that the use of coarse RA led to an improvement in the abrasion resistance. It was also shown that the use of seawater in the composition of mixes evidently influences the results of abrasion resistance. In mix P-CP-100, the abrasion resistance reached an increase of 22% with respect to the RC. This mix showed the best result, while P-CS-0 showed the worst one (decrease of 15%), but possibly due to an experimental error. Thus, it is possible to conclude that the use of coarse RA improves the abrasion resistance, due to the better bond between the cementitious paste and the coarse RA.

The mechanical tests results are summarized in Table 3, in terms of the variations relative to the RC.

Mix	Water absorption by	Water absorption by	Carbonation	Chloride ions	Shrinkage at 91
	immersion at 28 days	capillarity at 28 days	depth at 28 days	penetration at 28	days
				days	
P-CP-0 (RC)	- (10.5%)	- (2.98E-03 g/mm ²)	- (5.1 mm)	- (16.0E-12 m ² /s)	- (-70.1 μm/m)
P-CP-50	+20%	+4	+3	+15	+94
P-CP-100	+46	+30	+9	+25	+95
P-CS-0	0	+1	-65	+9	
P-CS-50	+17	+18	-65	+19	
P-CS-100	+49	+43	-51	+62	
S-CP-0	+10	-6	+19		+62
S-CP-50	+29	+11	+21		+183
S-CP-100	+53	+39	+34		+374
S-CS-0	+10	+5	-41		
S-CS-50	+23	+19	-63		
S-CS-100	+50	+44	-47		

Table 3: Results of the durability tests

The use of seawater in the composition caused an increase in water absorption by immersion, relative to concrete with freshwater. The mixes with RA were shown to be slightly less affected than those without RA. Compared to curing with freshwater, no clear effect of the effect of seawater on concrete curing was observed. A possible justification for this phenomenon may be related to the test method followed, where all mixes were immersed in freshwater. After 7 days of curing, the mixes cured with seawater developed a layer of crystallized salts on their surface. This layer may have been dissolved during the test, destroying a possible protective barrier to the entry of water into concrete.

The use of seawater in the composition caused an increase in water absorption by capillarity, compared with the mixes with freshwater. Although in mixes with 0% RA no clear trend was observed, in those with 50% and 100% of RA, this increase was 7% in mixes cured with freshwater and considerably lower in those cured with seawater. In this investigation, the effective water/cement ratio of concrete with seawater was higher than that of concrete with freshwater, which may justify the higher water absorption by capillarity of the former compared to the latter.

The use of seawater in the composition caused an increase in carbonation depth, relative to the mixes with freshwater. In mixes with 0% of RA, this increase was 19%, while in those with 50% and 100% of RA, it was found that this property's increase changed to 17% and 23%, respectively. However, curing with seawater revealed better resistance to carbonation of concrete, compared to that cured with freshwater. This



decrease in the carbonation depth of concrete cured with seawater, compared to concrete cured with freshwater, may be associated with the formation of a layer of crystallised salts, due to seawater curing, making it difficult for CO_2 to enter concrete.

The chloride migration test at 28 days was inconclusive in terms of the effect of seawater in the composition. The silver nitrate solution may have reacted with the chlorides, derived from the seawater in the composition, and with the chlorides introduced by the migration test, which made it impossible to measure the depth of chlorides in the mixes with seawater. Therefore, it was possible to conclude that the seawater curing increased the chloride migration coefficient, compared with the mixes cured with freshwater. This increase may be related to the higher water absorption by capillarity of concrete cured with seawater, compared to the one cured with freshwater. In mixes with 0% of RA, this increase was 10%. However, in those with 50% and 100% of RA, this increase was 4% and 31%, showing a substantial increase of variation with the increase of RA in concrete. Due to this inconsistency, it was not possible to conclude which of the mixes, with or without RA, was more affected by seawater curing.

The effect of seawater on concrete curing was not studied for concrete shrinkage, because the curing process designated for this investigation was not compatible with the test procedure adopted.

The use of seawater in the composition caused an increase in concrete shrinkage, compared to concrete with freshwater. In this research, the effective water/cement ratio of concrete with seawater was higher than that of concrete with freshwater, which may justify the higher shrinkage of the former compared to the latter. In mixes with 0% of RA, this increase was on average 35%, while in those with 50% and 100% of RA, this increase decreased to 41% and 29%, respectively. The increase in shrinkage seems to influence in the same way concrete with and without RA.

4. Conclusions

Based on the results of this research, the following conclusions were obtained:

- To obtain a constant workability, it was necessary to adjust the w/c ratio as the percentage of RA increased. However, the effective w/c ratio was always maintained. On the contrary, it was necessary to increase the effective w/c ratio due to the replacement of potable water with seawater;
- As the replacement ratio of NA with RA increased, compressive strength decreased. In concrete with potable water in its composition, curing with seawater decreased the compressive strength at all ages and at any replacement ratio. The seawater curing of concrete with potable water in its composition decreased its compressive strength. This effect is due to the formation of gypsum that causes expansive pressure;
- Tensile strength tended to decrease with increasing replacement ratio of NA with RA, due to the high content of ceramic RA present in CDW. In mixes with seawater in their composition, curing in seawater decreased their tensile strength compared to curing with potable water;
- As the percentage of RA increased, the modulus of elasticity decreased. The modulus of elasticity did not seem to vary with the type of curing, but decreased slightly with the use of seawater in the concrete composition, due to internal cracking of the concrete caused by chloride ions present in the seawater;
- The abrasion resistance increased with the replacement ratio of NA with RA in all mixes. This can be justified by the high adherence between the cement paste and RA. By using seawater in concrete, a slight deterioration trend in abrasion resistance was observed;



- The use of seawater in the composition caused an increase in water absorption by immersion, compared with the mixes with freshwater. The mixes with RA were shown to be slightly less affected than those without RA. Compared to curing with freshwater, no clear effect of the effect of seawater on concrete curing was observed;
- The use of seawater in the composition caused an increase in water absorption by capillarity, compared with the mixes with freshwater. This result can be justified by the higher effective water/cement ratio of concrete with seawater, compared with the concrete with freshwater;
- The use of seawater in the composition caused an increase in the carbonation depth, compared with the mixes with freshwater. However, curing with seawater decreased the carbonation depth, compared to that cured with freshwater. This can be associated with the formation of a layer of crystallised salts, due to seawater curing;
- The seawater curing increased the chloride migration coefficient, compared with the mixes cured with freshwater. This increase may be related to the higher water absorption by capillarity of concrete cured with seawater, compared to the one cured with freshwater. It was not possible to conclude which of the mixes, with or without RA, was more affected by seawater curing;
- The use of seawater in the composition caused an increase in concrete shrinkage, compared to concrete with freshwater. The increase in shrinkage influenced in the same way concrete with and without RA.

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LIFE CYCLE ASSESSMENT AND LIFE CYCLE COST ANALYSIS OF CONCRETE PAVEMENTS MADE WITH MIXED RECYCLED AGGREGATES AND OLIVE BIOMASS BOTTOM ASH

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Abstract

Energy demand and CO_2 emissions from the construction sector continue to rise. To face the global challenge of climate change, a transformation is required with solutions that incorporate sustainable materials. Finely-ground recycled materials such as mixed recycled aggregate from construction and demolition waste and olive biomass bottom ash can be used as supplementary cement materials. This research evaluates the environmental impact and the costs associated with the incorporation of recycled materials as a replacement for cement and natural aggregates in concrete pavements. Life cycle assessment and life cycle cost methodologies were applied to concrete pavement mixtures made from recycled materials. Life cycle assessment results showed that CO_2 emissions decreased with the incorporation of recycled materials, mainly due to the substitution of cement. In addition, life cycle cost results indicated that costs were reduced due to the use of recycled materials.

1. Introduction

Cement is the component of concrete that contributes the most to its environmental impact and economic cost, as a consequence of CO₂ emissions and energy consumption produced during clinker calcination [1]. Within the current context of the circular economy, recycled materials with a high clay composition such as mixed recycled aggregates (MRA) [2] and biomass bottom ash (BBA) [3] can be included as a replacement for cement with a prior crushing process, without including a calcination process. Concrete pavement for low-intensity or rural roads requires fewer quality requirements, allowing the use of recycled materials to replace natural aggregates [4]. Hence, the use of MRA and BBA in concrete pavements as a replacement for cement and natural aggregates can reduce the environmental loads and costs associated with the material. Life cycle assessment (LCA) makes it possible to quantify the environmental impacts associated with a product, as well as to identify the processes that significantly contribute to it [5,6]. Life cycle cost (LCC) is the total cost of a construction or its parts throughout its life cycle [7,8]. The joint



application of LCA and LCC could be very useful to choose the most sustainable option [9]. Thus, the main objective of this study has been to determine the environmental and economic feasibility of concrete pavements manufactured with MRA and BBA as a replacement for cement and natural aggregates.

2. Materials

Three concrete pavement mixtures were evaluated to determine the environmental impact and economic cost associated with their manufacture. The materials used in concrete pavements, the dosages and properties of the concretes are listed below.

2.1 Components of concrete pavements

The following materials were used for the concrete pavement mixtures.

- Cements used were cement EN 197-1 CEM II/A-L 42.5 N and cement EN 197-1 CEM I 42.5 R.
- Natural aggregates came from a dolomitic quarry located in Córdoba. Three fractions were used in the manufacture of concrete: coarse natural aggregate (CA), medium natural aggregate (MA) and fine natural aggregate (FA).
- Recycled materials were included in this study to replace cement and natural aggregates in concrete pavement production. MRA produced by a construction and demolition waste company and BBA from a biomass power plant were used as natural aggregates replacement. BBA and MRA were subjected to a crushing and screening process to obtain powder for cement substitution, that is, crushed BBA (pBBA) and crushed MRA (pMRA).
- A commercial superplasticiser admixture (SP) was included in the dosage. Its main function was to reduce the water demand of concrete with recycled materials due to the high water absorption capacity of these materials.

The main characteristics of component materials are shown in Table 1.

PROPERTY	MATERIALS										
	CEM I	CEM II	pBBA	pMRA	СА	MA	FA	MRA	BBA		
Density (kg/m ³)	3070	3110	-	-	-	-	-	-	-		
Size (mm)	-		0-0.125	0-0.125	12-22	4-12	0-4	0-22	0-4		
Density-SSD (kg/m ³)	-	-	2840	2910	2660	2640	2540	2370	1940		
Water absorption (%)	-	-	20.96	9.01	0.44	0.47	0.72	6.49	19.82		

Table 1: Properties of materials



2.2 Concrete pavement

The concrete pavement mixtures evaluated were: i) Control: a concrete pavement with conventional cement and natural aggregates; ii) Echohybrid-1: a concrete pavement with pMRA and pBBA as supplementary cement materials; iii) Echohybrid-2: a concrete pavement with pMRA and pBBA as supplementary cement materials, and replacement of natural aggregates by MRA and BBA. The dosages of the concrete pavement mixtures and their mechanical properties are shown in Table 2.

CONCRETE PAVEMENT			MECHANICAL PROPERTIES (MPa)										
	CEM II	CEM I	pBBA	pMRA	CA	MA	FA	MRA	BBA	Water	SP	Compressive strength	Flexural strength
Control	365	-	-	-	915	325	625	-	-	153.3	-	55.7	5.68
EcoHybrid-1	-	256	23	69	915	325	625	-	-	162.3	-	49.1	5.38
EcoHybrid-2	-	256	23	69	600	170	460	472	80	199.3	3.8	43.0	4.56

Table 2: Dosages and mechanical properties of the concrete pavement mixtures

3. Experimental methods

3.1 Life cycle assessment (LCA)

The environmental evaluation of the concrete pavement mixtures was carried out to determine the impacts associated with their manufacture. LCA was applied following the regulatory framework established in ISO 14040 and ISO 14044 standards [5,6] and the recommendations of the UNE-EN 15804:2012+A2 standard [10]. The system boundaries included the production of the component materials of concrete pavements, as well as the manufacturing process of the concrete at plant. The functional unit considered was the manufacture of one cubic metre of concrete. The life cycle inventory was generated taking into account the following considerations:

- For natural aggregates and recycled materials, primary data related to the consumption of raw materials, machinery and energy was collected, taking the year 2021 as a reference and with the processes of the Ecoinvent v.3.08 database [11].
- For cement, admixture and water, processes of Ecoinvent database v.3.08 [11] were used.

The data quality requirements related to technical, geographical and technological representativeness were met by adapting Ecoinvent database v.3.08 [11] processes with the data provided by the producers. In addition, electricity consumption was adapted to the process of the Spanish electricity grid.



The inventory data were processed in the SimaPro 9.4.0.49 software [12], applying the EN 15804+A2 Method V1.02 impact assessment method [13].

3.2 Life cycle cost (LCC)

LCC was developed following the methodology of EN 60300-3-3 standard [8] according to the structure established by the regulatory framework for the application of LCA. The system boundaries and the functional unit corresponded to those indicated for LCA. The inventory phase of LCC was developed using PYTHON language with the following cost structure:

- For natural aggregates and recycled materials, the costs were obtained by direct cost and indirect cost. Direct cost included amortization, operation, maintenance and energy consumption cost (by diesel or electricity) by machinery. Indirect cost included general expenses and industrial profit. It was calculated as a percentage of direct costs following the DELPHI methodology carried out with experts.
- The cost of cement, admixture and water were obtained directly from market values.

Also, externalities were included for all the materials to take into account the social costs due to the environmental cost. Environmental Prices V1.02/European Environmental Prices method (2015) [14] was adopted to calculate them by SimaPro 9.4.0.49 software [12].

4. Results and Discussion

4.1 LCA results

Table 3 shows the characterisation results obtained for the Climate Change category indicator. As can be seen, CO_2 eq. emissions associated with concrete pavements made from recycled materials decreased. The reduction was 11.4% when pBBA and pMRA were used to replace cement (Ecohybrid-1) and 9.7% when recycled materials were also incorporated as a replacement for natural aggregates (Ecohybrid-2). In this case, the benefit generated by the use of recycled materials was offset by the charges associated with the admixture added to the dosage. The production of recycled materials required minimal processing, resulting in less environmental impact [15].

CONCRETE PAVEMENT	CEM II	CEM I	pBBA	pMRA	CA	MA	FA	MRA	BBA	Water	SP	Manufa- turing	TOTAL
Control	252.43	-	-	-	0.96	0.35	0.67	-	-	0.03	-	4.45	258.89
EcoHybrid-1	-	222.60	0.03	0.34	0.96	0.35	0.67	-	-	0.04	-	4.45	229.43
EcoHybrid-2	-	222.60	0.03	0.34	0.63	0.18	0.49	0.38	0.04	0.05	4.52	4.45	233.71

Table 3: Characterisation results for the Climate Change category indicator (kg CO₂ eq.)



4.2 LCC results

The distribution of direct costs and indirect costs (D+I) and externalities (E) of the concrete pavement mixtures in euro/m³ are listed in Table 4. As can be seen, the inclusion of supplementary cement materials in concrete pavements decreased the cost by 14% due to the lower production cost of recycled materials compared to cement [16]. This reduction was somewhat less (13.8%) when natural aggregates were also replaced by recycled materials, due to the addition of admixture in the dosage as indicated in the previous section.

		-											-, ,		
CONCRETE PAVEMENT		CEM II	CEM I	pBBA	pMRA	CA	MA	FA	MRA	BBA	Water	SP	Manufac- turing	Partial	TOTAL
Control	D+I	34.75	-	-	-	4.54	2.10	5.74	-	-	0.19	-	14.20	61.54	98.02
	Е	33.22	-	-	-	0.40	0.14	0.28	-	-	0.01	-	2.43	36.48	
EcoHybrid-1	D+I	-	24.38	0.06	0.95	4.54	2.10	5.74	-	-	0.20	-	11.40	49.38	84.26
	Ε	-	31.48	0.01	0.13	0.40	0.14	0.28	-	-	0.01	-	2.43	34.88	
EcoHybrid-2	D+I	-	24.38	0.06	0.95	2.98	1.10	4.22	2.48	0.16	0.25	0.46	11.12	48.18	84.51
	Е	-	31.48	0.01	0.13	0.72	0.21	0.20	0.17	0.01	0.02	1.55	2.43	36.33	

Table 4: Cost distribution of concrete pavement mixtures (euro/m³)

5. Conclusions

Based on the results obtained, the following specific conclusions are presented:

- The use of pMRA and pBBA to replace cement in concrete pavement reduces CO₂ emissions up to 11.4% and the cost of the material decreases 14%.
- In addition, if natural aggregates are replaced by MRA and BBA, CO₂ emissions and the cost of the material are reduced to 9.7% and 13.8%, respectively.

The application of LCA and LCC methodologies confirms the economic and environmental feasibility of the use of recycled aggregate from construction and demolition waste and olive biomass bottom ash as a replacement for cement and natural aggregates in sustainable concrete pavements.

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INFLUENCE OF ACCELERATORS IN CEMENT MORTARS USING FLUID CATALYTIC CRACKING CATALYST RESIDUE (FCC): ENHANCEMENT IN MECHANICAL PROPERTIES AT EARLY-CURING AGES.

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Abstract

Supplementary cementitious materials (SCM) have been used in the construction industry mainly to reduce the greenhouse gas emissions associated with Portland cement. Among SCM, the fluid catalytic cracking catalyst residue (FCC), a waste from the petrochemical industry, is recognized by its high reactivity. Nevertheless, binders produced using SCM usually present low mechanical strength at early curing ages. This study aims to assess the effect of different accelerator additives (KOH, sodium silicate, and commercial additive) on the mechanical strength of mortars containing FCC. The results showed that after only 8 hours of curing, FCC mortars containing commercial additive presented a compressive strength gain over 100% compared to FCC mortar without additive (26.0 vs. 12.8 MPa).

Keywords: pozzolan, accelerator, compressive strength

1. Introduction

The construction industry is responsible for consuming significant amounts of raw materials, and Portland cement manufacturing produces around 7-8 % of anthropogenic CO2 [1]. For decades, the study on supplementary cementitious materials (SCM) has demonstrated their viability as partial replacements for Portland cement (PC), providing technological and environmental benefits [2]. The most used SCM are fly ash (FA), silica fume (SF), or blast furnace slag (BFS), which have been used in the cement industry. The use of fluid catalytic cracking catalyst residue (FCC) has been studied since the late 90s by various research groups worldwide [3-6]. In the first investigation of this waste, Payá et al. [6] demonstrated the importance of previous FCC grinding to enhance the pozzolanic reactivity. Moreover, the optimal percentages of cement substitution by FCC are in the 15-20% range and it was observed enhanced performance using FCC replacing sand in the dosage of mortars. Pacewska et al. [5] compared the use of the FCC with SF and FA in pastes, concluding that pastes with FCC reached double the compressive strength of control, and the FCC had better behavior than the other two pozzolans. Lu et al. [7] recently produced high-performance, high-speed 3D concrete printing (3DCP) using FCC. According to the authors, the use of FCC contributes to reducing CO2 emissions by up to 21.45% and the costs by about 18% compared to control. Besides good



performance for long curing times, the production of prefabricated specimens requires high compressive strength at early-curing ages. This technological demand is usually associated with thermal curing and/or the use of accelerator additives. In the literature, different materials have been used as accelerator additives, including commercial additives which present enhanced performance when compared to other materials [8-10]. (Habib Lone et al., 2015; Smaoui et al., 2005; Wang et al., 2022). Hence, in this study, the effect of accelerator additives (KOH, sodium silicate, and commercial additive) will be tested for mortars where FCC replaces partially sand in 10 wt.%. The compressive strength is assessed for 8, 24 and 48 hours, and for 28 curing days.

2. Materials and methods

The materials employed to fabricate the mortars were cement CEM I-52.5 R supplied by Cemex (Buñol, Spain) and FCC supplied by BP-Oil (Grao de Castellò, Spain). FCC was ground for 20 minutes in a Gabrielli Mill-2 equipment using 98 alumina balls. As accelerators were used, a solution of KOH 0.045M, sodium silicate (SIL, 64% H2O, 28% SiO2, 8% Na2O), and a commercial accelerator called Sika Rapid-1 (SKR) (Sika Spain). A superplasticizer was used to obtain mortars with an optimum workability value (110-120 mm) (Sika Viscocrete-5980). The mortars fabricated had 1/3 cement/sand ratio and 0.45 water/cement ratio. The sand employed had siliceous nature. The FCC replaced 10% of the weight of sand, maintaining constant the quantity of cement. The method of the mixture and the assay of compressive strength followed the steps indicated in the Spanish standard [11]. (UNE EN-196-1, 2018). The composition and nomenclature of the mortars are shown in Table 1.

	Cement (g)	Sand (g)	Sand replacing * (g)	Accelerator (g)	H ₂ O (g)	Plasticizer. (g)	Workability (mm)
CON	450.0	1350.0	-	-	202.5	-	110
FCC	450.0	1215.0	135.0	-	202.5	3.2	110
CON+KOH	450.0	1350.0	-	9.0	202.5	1.1	111
FCC+KOH	450.0	1215.0	135.0	9.0	202.5	6.2	119
CON+SIL	450.0	1350.0	-	9.0	202.5	1.2	112
FCC+SIL	450.0	1215.0	135.0	9.0	202.5	5.7	113
CON+SKR	450.0	1350.0	-	9.0	202.5	-	113
FCC+SKR	450.0	1215.0	135.0	9.0	202.5	3.2	116

Table 1: Dosage of mortars

* Sand, respect to the control mortar (CON), was replaced by mineral addition (FCC) 10% by mass.



3. Results and discussion

The curing ages chosen to perform the compression test were 8, 24, and 48 hours of curing to evaluate the early-curing ages, and 28 days to evaluate the influence of the accelerating additive on the long-term curing age. The values of compressive strength for the different ages of curing are shown in Table 2.

	8 h	24 h	48 h	28 d
CON	6.85	29.23	34.47	56.96
FCC	16.18	39.93	55.44	88.54
CON+KOH	7.51	24.60	28.86	48.13
FCC+KOH	17.86	48.13	52.98	68.10
CON+SIL	7.56	35.42	40.69	61.25
FCC+SIL	13.83	47.72	60.38	89.30
CON+SKR	12.76	38.67	40.40	64.16
FCC+SKR	26.03	50.61	60.43	91.60

Table 2: Compressive strength (MPa) of mortars at different curing age
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To quantify the contribution of the accelerator additives and the FCC, the Resistance Activity Index (RAI) value is calculated between each of the mortars and the control mortar without any type of accelerator or mineral addition. Figure 1 represented the values for each accelerator.



Figure 1: Values of RAI for the different hardening accelerator additives.



4. Conclusions

From the results obtained, it can be concluded that:

- The SKR accelerant is the additive with the best behavior, especially in the first 8 hours of curing, without reduction on the strength for long curing age (28 days). There is a synergic effect between FCC and SKR.
- KOH appears to be beneficial in the mortar with FCC only until the first hours of curing, approaching 48 hours do not exert any benefit over FCC mortar.
- Unlike mortar with KOH, mortars with SIL improve the compressive strength containing FCC from 24 hours of curing.
- Mortars containing FCC for the curing age of 28 days obtain compressive strength values greater than 88 MPa, except the one containing KOH. These values confirm that the FCC is a SCM with excellent pozzolanic activity.
- The KOH, after 48 hours, reduces the compressive strength of mortars. The other accelerators get values higher than the controls and are very similar to them.

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SUSTAINABLE MORTARS REUSING AGRICULTURAL WASTE

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Abstract

The use of secondary raw materials for recovery in construction materials is scientifically proven. However, due to the difficult technical feasibility of the products obtained because of the limitations established in their own regulations, the application on a real scale of the solutions obtained is highly compromised. In this sense, masonry mortars are a construction material that allows the incorporation of different secondary raw materials or by-products from different industrial activities as they have low requirements.

For these reasons, this preliminary study on the technical feasibility of the recovery of olive stone in masonry mortars is proposed. To this end, a conventional mortar, as a reference, and a mortar manufactured with the incorporation of one type of olive stone, called Piropel, (P) replacing 10% and 20% of natural sand by volume, in accordance with the UNE EN 998-2 standard. The properties of consistency, density and air content, when fresh, and density, water absorption by capillarity and mechanical resistance, when hardened, were tested. It was found that the results obtained were favourable as long as the amount of replacement was up to 10%. Therefore, these mortars would be suitable for masonry applications, contributing to introduce the construction sector in the field of sustainability and circular economy.

1. Introduction

The construction industry has a significant economic and environmental impact [1]. Moreover, the sector is a major consumer of resources, using around 50% of raw materials and consuming 36% of global final energy use [2,3]. The sector also stands out in terms of the large amount of harmful emissions into the environment (23%), mainly CO_2 emissions [4] and the large amount of waste generated, some 10 billion tonnes of waste per year [5].



The use of secondary raw materials in the manufacture of masonry mortar can be an opportunity for the sector in order to reduce the consumption of natural resources, water and energy as well as waste and emissions to the environment according to the circular economy strategy [6-11].

Olive stone is considered a by-product of the olive industry and have a high presence in the countries of the Mediterranean arc and specifically in Andalusia. Therefore, its possible recovery in masonry mortars for construction would represent a double contribution to sustainability due to the environmental benefit it would bring to both the construction and olive-growing sectors.

The aim of this work is to study the technical feasibility of using olive stone to replace conventional sand in masonry mortars and evaluate its mechanical properties in fresh and hard state.

2. Materials

Portland Cement type CEM I 42.5 R-SR 3, provided by "Cementos Portland Valderrivas, S.A." located in Alcala de Guadaira, Seville, Spain has been used.

The filler applied has a limestone-dolomitic nature, with a density of 2.77 kg/m³, crushed material supplied by "Triturados Puerto Blanco", company placed in Granada, southern Spain.

Limestone-dolomitic natural sand (NS), 0/4 mm size provided by a quarry located in Granada, southern Spain has been used. This material meets the requirements of the aggregates standard UNE EN 13139 and its density is 2.77 g/cm³.

The olive stone studied has been Piropel type, provided by Peláez Renovables S.L. company with 0.5/4 mm size, 21.23% water absorption and a density of 1.34 g/cm³.

The admixture used has been a Superplastifizer MASTERERASE 3530 from Master Builders Soutions with a density of 1.06 g/cm³ and tap water from the city of Granada has been used to cast the mortars.

3. Experimental methods

3.1 Mortars manufacturing

The dosage chosen to manufacture the mortars consists of a cement-sand ratio of 1:8, a water-cement ratio of 1.2, 13% filler (on the weight of the aggregate) and 1% additive (on the weight of the cement). The study Mortars, P-10 and P-20 have a replacement of a 10% and a 20% respectively of sand by pre-saturated olive stone. The material has been pre-saturated 24 hours before the mortar manufacture. A Reference Mortar, RM, to have a direct comparison, was casted, with the same proportions, excluding the olive stone. Dosages are shown in Table 1.


Mortars	Sand (g)	Filler (g)	Pre- saturated Olive stone (g)	Cement (g)	Water (g)	Admixture (g)
RM	2657.50	345.50	0.00	328.00	393.60	3.28
P-10	2391.72	345.50	155.85	328.00	393.60	3.28
P-20	2125.97	345.50	311.70	328.00	393.60	3.28

Table 1. Mortars dosages

The mortars under study were manufactured according to the harmonised standard UNE EN 998-2 [12] and their consistency, density and occluded air were determined in fresh state, and water absorption by capillarity, density and mechanical strength in hardened state.

4. Results and Discussion

Table 2 summarises the results of the tests carried out on the mortars in fresh state (consistency, bulk density and occluded air content), capillary water absorption coefficient and bulk density in hardened state.

Mortas	Consistency (mm)	Fresh state bulk Density (kg/m ³)	Air content (%)	Water absorption by capillarity (g/m ² x min 0.5)	Hard state bulk Density (kg/m ³)
RM	138.00	2293	4.35	0.70	2187
P-10	170.50	2201	4.40	0.48	1975
P-20	171.85	2102	4.10	0.42	1902

Table 2. Results of mortars test

The **consistency** of the mortars in fresh state is the parameter that determines the workability required to place them on site. The mortars produced showed results within the recommended normative range of plastic consistency (140-200mm) [13]. In both cases of replacement, it has been found that the incorporation of olive stone has been a determining factor in the consistency, improving the workability of the mortars with olive stone in relation to that of the reference mortar.



The **bulk density** of mortars in fresh state is related to the density of their component materials and to their air content, so that the lighter they are, the more workable they are [13]. As expected, it can be seen that mortars with the replacement of conventional sand with olive stone have reached lower densities than conventional mortar which can be an advantage when spreading the mortar or in order to isolate (thermally or acoustically)

The **air content** test provides indirect information on the workability of the mortars, since the higher the air content, the greater the workability, as it acts as a plasticity-enhancing agent [13]. The air content generated in the mortars tested is generally low and quite close to that of the reference mortar, which can be attributed to several aspects such as the use of a specific plasticising additive that has not contributed to the formation of air bubbles in the fresh paste.

Water absorption by capillarity is performed to indirectly measure the durability of the mortar through its permeability, which can cause a flow of particles and/or salts that is undesirable for the durability of the construction element. This property depends on the porous structure of the material, so the greater the compactness, the lower the water absorption [13]. Contrary to expectations, the mortars substituted with 10% and 20% respectively present a lower absorption coefficient than the reference. These results could be attributed to the porous network generated by larger and/or less intercommunicated pores that would prevent water rising by capillarity, favouring the use of this type of mortar in more humid climatic environments.

Related to the reference mortar, the study mortars with olive stone had a lower **bulk density** value than the reference one. These results should be understood in a positive way, as in fresh state, since mortars made with olive waste can contribute to the thermal insulation of buildings while also decreasing the weight conferred to the structure [14, 15].

Table 3 summarises the results of the mechanical flexural and compressive strengths of the mortars manufactured at 7, 14 and 28 days.

	Flex	cural strengths (M	/IPa)	Compressive strengths (MPa)					
	7d	14d	28d	7d	14d	28d			
RM	4.01	4.64	4.48	16.06	17.75	17.58			
P-10	1.512	2.222	3.541	5.516	8.536	10.028			
P-20	0.230	0.485	2.396	0.491	0.582	1.080			

Table 3. Flexural and compressive strengths

As expected, in both cases the mechanical strengths of the mortars tested were reduced as the substitution percentages increased. In the mortar with a 10% substitution the decrease is not as high as in the 20% substitution mortar in which the strength falls by more than 40%



5. Conclusions

Based on the tests carried out, we can confirm the feasibility of incorporating olive pits for the manufacture of masonry mortars as a secondary raw material, contributing to sustainability, the environment and the circular economy. In particular, in fresh state, the influence of the olive stone content has been observed, with appreciable and expected changes in consistency, density and air content. In hardened state, an expected influence in terms of the lower density of the mortar depending on the amount of natural sand substituted has been shown. These results will influence both the weight given to the structure and its expected better thermal behaviour.

The mechanical strength has been affected by the amount of granular material substituted, with lower differences for the 10% substitutions with respect to the reference mortar, and unacceptable results for 20% substitution, which lead us to confirm that this type of olive stone could be used up to 10%.

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APPLICATION OF DIFFERENT TECHNIQUES OF MECHANICAL AND ALKALINE ACTIVATION OF BIOMASS BOTTOM ASH FOR USE IN MORTARS

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Abstract

Geopolymers are sustainable materials based on precursors, which can come from waste and by-products, are alkaline-activated and can become the medium-term future of the cement manufacturing industry. In this study, the application of different activators on biomass bottom ash for use in mortars has been studied. The results obtained have made it possible to determine the effectiveness of two types of activators, Sodium Hydroxide and Sodium Metasilicate, obtaining positive results, and also optimising different combinations of olive biomass bottom ash and blast furnace slag.

1. Introduction

A geopolymer is defined as a solid material formed with aluminosilicates and by activation of alkali silicates as precursors. Geopolymers are also often described in the literature as "mineral polymers" and "inorganic polymers"[1]. However, the terms geopolymers and inorganic polymers are gaining popularity within the field of academic research.

The main process difference between ordinary Portland cement (OPC) and geopolymer is that OPC is based on a manufacturing process that imparts high potential energy to the material through calcination. This means that the activated material will readily react with a low energy material such as water [2,3]. In contrast, geopolymer uses very low energy materials, such as fly ash, slag and other industrial waste, and a small amount of high chemical energy materials (alkaline activators) to react only on the surface of the particles and act as a binder paste.

The use of geopolymers instead of traditional Portland cement provides two significant environmental benefits: the first is the reduction of CO2 and the second is the use of recycled industrial waste, which means less extraction of raw materials [4-6].

This study shows an advance in knowledge on the alkaline activation of wastes such as olive biomass bottom ash and blast furnace slag by applying different precursors and evaluating the mechanical properties acquired by the geopolymer pastes. Furthermore, the application of this alkaline-activated waste in the



manufacture of mortar has been studied, thus providing a new sustainable and innovative design and construction option that reduces CO2 emissions and reuses waste.

2. Properties of Materials

2.1 Cements and Natural Sand

In this work, CEM I 42.5 was used; this cement does not contain mineral additions. Therefore, the behaviour of the mortar with the addition of other waste is not conditioned by the components present in the cement. The water used was potable water, and CEN Standard Sand (NS) was used.

2.2 Biomass Bottom Ashes (BBA)

Biomass Bottom Ash (BBA) is a by-product generated from the combustion of biomass from different industries, composed mainly of olive pomace. BBA is a heterogeneous mixture of particles of different sizes, composed of ash and unburned or partially burned biomass. The origin of the biomass used and the technology used to burn it have a great influence on the characteristics of the BBA.

BBA used in this study comes from the thermal power plant located in Puente Genil, Cordoba (Spain). BBA was obtained from the combustion of various agricultural wastes, e.g., olive prunings and other plant materials.

2.3 Ground Grnulated Blast-Furnace Slag (GGBFS)

Ground Granulated Blast-Furnace Slag (GGBFS) is a by-product from the cooling of cast iron slag. It has been used previously in the manufacture of cements as it is able to limit the heat of hydration of the cementitious material. Its chemical composition depends on the raw materials used in the iron manufacturing process, containing mainly calcium, silicon and aluminum oxides. The rapid cooling of this by-product makes it very amorphous, which benefits alkaline activation.

In this case, Ground Granulated Blast-Furnace Slag from the Lafarge Holcim Company, Carbonera Almeria (Spain), was used.

3. Mix proportions and manufacture of mortars.

Six mixes of binder pastes were manufactured using sodium hydroxide (NaOH) as the main activator providing an alkaline environment, in accordance with previous research [7] and sodium metasilicate (Na2SiO3) as a secondary activator to provide the mixtures with increased silica (SiO2). Table 1 and 2 show the different mixes manufacture in the laboratory.



	GGBFS	BBA	ACTIVA	ATOR	H ₂ O
			NaOH	Na ₂ SiO ₃	
BBA 100	0	300 g	120 ml (8M)*	-	-
GGBFS 100	300 g	0	130 ml (8M)*	-	-
GGBFS 66/33 BBA	200 g	100 g	130 ml (8M)*	-	-
BBA 66/33 GGBFS	100 g	200 g	120 ml (8M)*	-	-
Meta S. BBA 66/33 GGBFS	100 g	200 g	31,2 g	58 g	120 ml
Meta L. BBA 66/33 GGBFS	100 g	200 g	31,2 g	82 ml (8M)*	40 ml

Table 1: Pastes binder mix proportion

*(8M): 8 Molar

Table 2 shows the mortars with the greatest potential for use according to their mechanical properties obtained in the pastes previously carried out.

	Table 2: Dosages of the mortars												
				MORTA	ARS Binder	Mix Pro	portions						
		CEM I 42.5	NS (g)	BBA – for NS	GGBFS (g)	BBA (g)	H ₂ O (ml)	ACTI	VATOR				
		(5)		(5)				NaOH	Na ₂ SiO ₃				
M1	CR- CEM I 42.5	450	1350	-	-		225	-	-				
M2	CR- CEM I 42.5 /BBA	450	945	405	-		225	-	-				
M3	BBA 66/33 GGBFS	315	1350	-	44.5	89	157.5	67.5ml (8M)	-				
M4	BBA 66/33 GGBFS - RS	315	945	405	44.5	89 g	157.5	67.5ml (8M)	-				
M5	GGBFS 66/33 BBA	315	1350	-	89	44.5	157.5	67.5ml (8M)	-				
M6	GGBFS 66/33 BBA-RS	315	945	405	89	44.5	157.5	67.5ml (8M)	-				
M7	CEM 50/50 (BBA 66/33 GGBFS) (Metha S.)	225	1350	-	76.5	148.5	275	23.2 g	28.7 g				
M8	CEM 50/50 (BBA 66/33 GGBFS) (Metha L.)	225	1350	-	76.5	148.5	230	23.2 g	40.6 ml				



4. Experimental methods and results

4.1 Compressive and flexural strength

The compressive and flexural strength were measured at 1, 7, 28 and 90 days according to UNE-EN 196-1. A hydraulic press was used to apply a load at a constant speed. Table 3 shows the results obtained for the different pastes manufactured.

	FLEX	URAL STR	ENGTH	COMP	RESSIVE STI	RENGTH					
		(MPa)		(MPa)							
	7 Days	28 Days	90 Days	7 Days	28 Days	90 Days					
BBA 100	0	0	0	1.8	3.29	3.4					
GGBFS 100	0	0	0	35.05	38.38	39.85					
GGBFS 66/33 BBA	0	0	0	14.65	38.08	39					
BBA-PG 66/33 GGBFS	0	3.81	0	14.96	32	16.75					
Meta S. BBA-PG 66/33 GGBFS	0	0	0	19.2	19.36	19.7					
Meta L. BBA-PG 66/33 GGBFS	0	0	0	52.3	76.8	62.9					

Table 3: Results of mechanical behaviour of pastes binder.

It can be seen how the introduction of GGBFS increases the mechanical strength of the pastes, possibly due to the extra silica and aluminium oxide, causing a higher activation in the mixture. Furthermore, the addition of sodium metasilicate makes the alkaline activation more efficient, again due to the increase in silica, especially when using the metasilicate in liquid form, obtaining the highest strength at 90 days.

		Table 4: Result	s of mechanica	l behaviour of	mortars.				
	FLEXU	RAL STRENG	FH (MPa)	COMPRES	COMPRESSIVE STRENGTH (MPa)				
	7 Days	28 Days	90 Days	7 Days	28 Days	90 Days			
M1	9.75	7.9	11.77	35	44.9	54.6			
M2	3.23	3.59	3.57	15.1	18.5	21.2			
M3	0	2.7	4.78	4.5	5.1	6.95			
M4	0	0	2.4	3.3	5.1	5.7			
M5	2.63	3.7	4.71	7.6	6.7	7.35			
M6	0	0	2.95	1.8	8.2	8.3			
M7	5.32	5.62	5.68	11.63	13.47	22.23			
M8	5.87	5.91	6.17	20.65	24.01	27.16			



As for the mechanical behaviour results obtained for the different mortars, table 4 confirms the results obtained for the pastes. Although the substitution of sand by BBA does not provide positive results (M2, M4 and M6), as the strength is slightly lower than the mortars without sand substitution, the addition of metasilicate does provide a considerable increase in strength. In the case of the activator (M8) with dissolved metasilicate, the strength is between three and four times greater than the rest of the mortars.

5. Conclusions

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

- The application of biomass bottom ash combined with blast furnace slag as activatable precursors has yielded positive results, making this mixture of processed by-products suitable for the production of geopolymers.

- The combination of blast furnace slag and biomass bottom ash plus an activator that provides an extra amount of silica increases the activation potential of these by-products.

- The combination of 66% biomass bottom ash and 33% blast furnace slag showed the best compression performance when sodium metasilicate was applied in solution. Compressive strength results have been substantially improved by using this silica input. These results could allow an industrial scale-up of this type of alkaline activated mortars using sodium metasilicate.

6. Aknowledgements

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PERFORMANCE OF SELF-COMPACTING CONCRETE FROM A NEW ECO-HYBRID ADDITION BASED ON MIXED RECYCLED AGGREGATES AND BIOMASS BOTTOM ASH

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Abstract

This study presents the successful viability of producing self-compacting concrete using a novel active mineral addition composed of a pulverised blend of olive biomass bottom ash and mixed recycled aggregates The results were compared to conventional active mineral addition, including silica fume, coal fly ash, and blast furnace slag, to validate its effectiveness. The results confirm the practicality of incorporating this new sustainable addition, as it enhances both the fresh properties of the concrete, which are crucial for self-compacting concrete, and the ultimate strength achieved.

1. Introduction

The application of new mineral additions to cement is crucial for advancing the development of sustainable cements and concretes. These additions typically originate from industrial by-products, clays, or volcanic materials [1,2]. In recent years, extensive research has been conducted to explore the utilisation of new waste materials and their derivatives as mineral additions in cement, with the aim of producing eco-friendly concretes.

Biomass bottom ashes, given their composition, have found various applications in cement-based construction materials [3]. Recent studies have focused on processing biomass bottom ash derived from forest residues, in order to obtain a suitable particle size that can be blended with cement as a supplementary material [4].

Likewise, the use of recycled aggregates from construction and demolition waste (CDW) in concrete production has been extensively research in recent years. The physical properties of recycled aggregates make them suitable for application as aggregates in concrete mixtures [5].

This study incorporates a combination of mixed recycled aggregates, composed by bricks, concrete, natural aggregates from CDW and olive biomass bottom ash to develop a new sustainable mineral addition to produce self-compacting concrete (SCC). The desired proportions of mixed recycled aggregates and biomass bottom ash are mixed and subjected to a grinding and micronisation process to achieve the desired fineness and particle size distribution.



Following the preparation of the novel eco-hybrid addition, self-compacting concretes were fabricated in the laboratory, and their consistency and strength properties were determined. Three conventional mineral additions, namely silica fume, coal fly ash, and blast furnace slag, were also investigated to assess and compare the obtained results.

2. Materials

2.1 Cement and natural aggregates (sand, aggregates, and filler)

Cement: The cement utilised for manufacturing SCC was CEM I 42.5R from Cementos Portland Valderrivas.

Natural aggregates: The natural aggregates were supplied by Áridos Troyano S.L. These aggregates are limestone-based, with a minimum calcium carbonate composition of 65%. Two fractions were used: sand with a particle size of 0/4 mm and gravel with a particle size of 4/12 mm.

Limestone filler: Betocarb F filler, supplied by Omya was applied. It is a fine ground calcium carbonate (<40 μ m) with a composition of 98% calcium carbonate and a specific surface area of 5 m²/g. This filler is specifically recommended for the manufacturing of SCC.

2.2 Conventional active additions: silica fume, coal fly ash, and ground granulated blast furnace slag

Three mineral active additions were applied in this study as reference materials for evaluating the properties of recycled materials. These additions include silica fume, coal fly ash, and ground granulated blast furnace slag.

Silica fume: The silica fume (SF) used in this study was sourced from FerroAtlántica S.A. Silica fume is a byproduct of silicon and ferrosilicon production, obtained through the combustion of silica sands in high-temperature furnaces. It consists of extremely fine particles of amorphous silica.

Coal fly ash: The coal fly ash (CFA) used in this study was obtained from the Palmones Thermal Power Plant in Cádiz, owned by Viesgo. The sample was provided by Cementos Portland Valderrivas. Fly ash is a byproduct of coal combustion in thermal power plants that utilize pulverised coal. It is generated during the combustion of pulverised coal in furnaces and captured by emission control equipment such as bag filters or electrostatic precipitators.

Ground granulated blast furnace slag: The ground granulated blast furnace slag (GGBFS) used in this study was sourced from Lafarge Holcim, Carboneras Almería. Blast furnace slag is a byproduct of steel production in blast furnaces, where iron ore is melted with coke and limestone. During this process, the slag forms as a floating layer on the molten metal and is subsequently removed for cooling and crushing.



2.3 Eco-hybrid addition: powdered biomass bottom ash and mixed recycled aggregate

Eco-hybrid (EcHy) addition was developed by Rosales et al. [6] from a mixture of 76% mixed recycled aggregates (MRA) and 24% olive biomass bottom ash (BBA), both pulverised. Mixed recycled aggregates from the treatment of construction and demolition waste were supplied by the Gecorsa treatment plant. Biomass bottom ash, a residue generated in the combustion chamber of a biomass combustion plant, was supplied by the Sacyr Valoriza plant.

3. Experimental methods

3.1 Concrete dosages and manufacturing

A control dosage was performed with 500 kg of powder (cement + filler) and a water-to-cement ratio of 0.43. A dosage of 5 kg/m3 of the superplasticiser additive MasterEase 5025 was applied. That dosage was performed to guarantee an adequate amount of "cement + water + fine aggregates" relation to achieve its self-compacting characteristics.

Following the control dosage, four mixtures were designed by replacing 15% of the cement with the studied additions (10% in the case of silica fume, the maximum allowed by regulations). Both the admixture content and the water-to-cement ratio were kept constant, except for mixture M5, with which it was necessary to increase the water-to-cement ratio to ensure the properties of the self-compacting concrete (SCC). This increase in the water-cement ratio was due to the high absorption of the eco-hybrid powder. Table 1 provides an overview of the mix proportions used in the development of all the mixtures in this study.

Name	Description	CEM	Filler	Sand	Aggregates	SF	CFA	GGBFS	EcHy	Add	Water	w/p (in mass)	w/p (in volume)
M1	Control	450	50	1120	580	-	-	-	-	5	216	0.43	1.32
M2	10% SF	405	50	1110	570	45	-	-	-	5	216	0.43	1.27
M3	15% CFA	382.5	50	1130	585	-	67.5	-	-	5	216	0.43	1.26
M4	15% GGBFS	382.5	50	1130	585	-	-	67.5	-	5	216	0.43	1.28
M5	15% EcHy	382.5	50	1125	570	-	-	-	67.5	5	241.5	0.48	1.40

Table 1: Dosages of the concrete mixtures

3.2 Fresh and hardened SCC properties

Two series of tests were conducted: tests on fresh concrete to determine its consistency and flowability properties, and tests on hardened concrete to determine its strength capacity.



Two tests were performance to analyse the consistency and flowability of SCC: **slump flow test**, according to EN 12350-8:2019 and **L-Box test** according to EN 12350-10:2010.

To determine the **compressive strength** of the developed SCC, 100 mm x 100 mm cubic samples were tested at ages 7, 28, and 91 days following the guidelines of EN 12390-3:2019.

In addition, a **tensile splitting strength** test was conducted on a 150 mm x 300 mm cylindrical specimen. The specimen was subjected to diametric compression for 7, 28, and 91 days, following the procedures outlined in EN 12390-6:2009.

4. Results and Discussion

4.1 Fresh SCC properties: Slump and L-Box

A consistency study is essential to produce SCC, due to the fact that its analysis allows to differenting a conventional concrete from a SCC. Table 2 shows the results obtained for the Slump test and the L-Box test.

According to the results for the two tests, all the mixtures are within the limits recommended by the Spanish regulations for the manufacture of SCC.

Analysing the data for the L-Box test, the use of CFA and eco-hybrid addition implies a decrease in viscosity, a behaviour consistent with the results obtained by other authors, who applied fly ash and biomass bottom ash [7,8].

		SI	ump Test	L-Box Test		
		t ₅₀₀ (s)	D (mm)	H ₂ /H ₁		
Compliand	Compliance requirements		550-850 mm	0.75 - 1.00		
M1	Control	3	775	0.85		
M2	10% SF	2	810	0.85		
M3	15% CFA	2	638	0.76		
M4	15% GGBFS	3	720	0.90		
M5	15% EcHy	3	730	0.76		

Table 2: Results of fresh SCC properties

4.2 Hardened SCC properties: Compressive and tensile splitting strength



The compressive and tensile splitting strength results for the different mixtures at various ages (7 days, 28 days, and 91 days) are presented in Table 3.

The control mix showed the highest strength performance, followed by the mixes with conventional additions (SF and GGBFS), which exceeded the strength of the control after 91d, due to their high pozzolanic capacity. The mix with the new ecohybrid addition (EcHy) and CFA showed slightly lower strengths, with drops of around 28% in strength at 28 days. However, these samples exceeded 40MPa, being very positive results.

		Compre	ssive streng	nt (MPa)	Tensile splitting strenght (MPa)			
	Mixtures	7d	28d	91d	7d	28d	91d	
M1	Control	46.90	59.53	60.63	3.36	3.97	5.30	
M2	10% SF	42.40	52.04	62.41	3.08	3.54	3.89	
М3	15% CFA	35.27	43.09	43.83	3.21	3.96	4.66	
M4	15% GGBFS	44.36	58.80	66.92	3.83	4.31	4.97	
M5	15% EcHy	38.42	42.34	47.17	2.53	2.74	2.90	

Upon analysing the data presented in Figure 1, it is evident that the eco-hybrid addition demonstrates notable changes and benefits in the strength mechanism of self-compacting concrete, despite a decrease in strength. In contrast to the control mixture, which relies primarily on hydraulicity for its hardening mechanism using CEM-I, the additions employed in the eco-hybrid addition continue to exhibit strength development beyond 28 days due to pozzolanic reactions. Remarkably, the eco-hybrid addition exhibits strength development comparable to that of fly ash between the 7 to 91-day period. Moreover, the observed increase in strength from 28 to 91 days is of a similar magnitude as observed in mixes M2 and M4, which utilise silica fume and blast furnace slag, respectively.



Figure 1: Increase in compressive strength at different ages



5. Conclusions

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

- The use of eco-hybrid addition implies a slight increase in the water-cement ratio, if the admixture content is not modified, to maintain the characteristics of an SCC.

- The consistency measured by the slump test is not affected by the eco-hybrid addition, apart from the flowability, which is within the allowed limits.

- The eco-hybrid addition allows similar strengths to be achieved at 28 days as the mix developed with fly ash, this material being widely applied in the manufacture of concrete.

- The strength values, both compressive and indirect tensile, increase steadily from 7 to 91 days, showing the pozzolanic character of the eco-hybrid addition.

In conclusion, the eco-hybrid addition is presented as an alternative material for the manufacture of selfbinding concretes, allowing characteristics that would be achieved with very extensive additions such as coal fly ash.

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ECO-CONCRETE TOWARDS SUSTAINABLE CONSTRUCTION

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Abstract

The development of concrete mixes that include recycled waste with active and predictive safety features is a possible approach mitigating the harmful impacts of the construction industry, such as CO2 emissions and the consumption of energy and natural resources during the construction of infrastructures. This study establishes the basis for formulating new smart materials towards a sustainable concrete. To this end, a comprehensive recycled pavement solution has been developed that combines eco-hybrid cement made with 25% mixed recycled aggregate powder (pMRA) and biomass bottom ash powder (pBBA) and a 50% substitution of natural aggregate by mixed recycled aggregates (MRA) and biomass bottom ash (BBA). The objective of this study is to ensure satisfactory rheology, mechanical strength and durability of eco-concrete manufactured from waste. For this purpose, six concrete mixtures have been carried out, analysed with different experimental methods, including conventional mixtures and mixtures with recycled materials, including structural fibres.

1. Introduction

Greenhouse gas emissions are a problem that has been mitigated for decades. Programs worldwide, both encouraging practices in the private sector and promoting research studies by governmental organizations, show a generalized encouragement to move towards global net-zero emissions. Initiatives dating back more than 25 years, such as the Kyoto Protocol [1], now obsolete, which puts the focus on the governments of different nations, or more current initiatives such as SBTi (Science Based Targets Initiative) [2], with practices based on the latest science and audits to corroborate the collaboration of companies with this goal [3], or Race to Zero [4], which brings together non-state actors, including companies, cities, regions, financial and educational institutions, to take action to halve global emissions by 2030.

Cement, a polluting element in CO2 emissions, represents about 10% of the mass of concrete, 4 Gigatonnes per year, the same amount as global food consumption [5]. Construction-related activities generate 7.7 Gigatonnes of CO2 per year, of which cement generates 36% of this final amount [6]. The processes that emit the most CO2 are hydrocarbons, related to clinker production [7]. As for aggregates, 17.5 Gigatonnes per year are included as gravel, grit and sand in the production of concrete [8]. Because of this, the use of supplementary cementitious materials (SCM) is of vital importance. Elements such as fly ash, blast furnace slag [9], calcined clay, replace part of the cement used in concrete mixes. It can be observed that calcined



clay presents better values, but, as the calcination temperature increases up to 900°C, the pozzolanicity decreases, and the drop in strength is more accentuated [10].

By increasing the degree of substitution and optimising the mixes, a 45% reduction in CO2 emissions can be achieved [7]. In addition, there are recycled materials, such as Construction and Demolition Waste [11] with a high composition of ceramics and Biomass Bottom Ash (BBA) [12] that can be included as cement substitutes with a previous crushing process, without including a calcination process.

	FRX (%)											
	CaO	SiO ₂	SO ₃	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	Density (g/cm ³)		
CEM II/AL 42.5	67.05	18.11	4.43	4.24	2.65	1.71	1.07	0.40	0.19	3.07		
CEM EcHy	55.94	22.15	4.39	5.08	2.82	1.57	1.21	0.40	0.23	2.91		

2. Properties of Materials

2.1 Cements

The conventional cement used in this research was CEM II 42.5. A new cement was developed in the scope of the project where is involved this communication, called Eco-Hybrid Cement [12]. This cement is made up of 75% CEM I 52.5, 19% mixed recycled aggregate powder and 6% biomass bottom ash powder. The above recycled material powders have been micronised to achieve a specific surface area in the cement range (5000 cm²/g) [13]. The physicochemical properties are summarised in Table 1.

Table 1. Physicochemical properties of cements.

The elemental composition showed similarities with other studies [14] where powders with high Al_2O_3 and Fe_2O_3 content were found to give competent pozzolanic and mechanical strength results. Elemental compositions are similar among cements.

2.2 Natural Aggregate and Waste Substitutes for Natural Aggregate

The natural aggregate came from a dolomitic quarry located in the municipality of Cordoba. The aggregates were divided into three parts depending on grain size: fine natural aggregates (0 - 4mm), medium natural aggregate (4 - 12mm) and coarse natural aggregate (12-22mm). To perform the characterisation of natural and recycled aggregate for concrete production the distinction between fine and coarse was made for the calculation of density and absorption. In addition, it is important to determine the amount of water to be added to the mixes, since the mixed recycled aggregate absorbs a large amount of water, which can subtract the water necessary for the hydration of the cement. Friability ratio, Sand equivalent, Aggregates Crushing Value and Los Angeles coefficient were calculated following the standards.



			Results			
Properties	Size	Natural Mixed Aggregate Aggregate		Biomass Bottom Ash	Test Method	
Density-SSD (g/cm ³)	0 - 4 mm	2590	2370	1.94		
Water Absortion (%)	_ • · · · · ·	0.72	9.42	19.82	UNF-FN 1097-6	
Density-SSD (g/cm ³)	4 - 22 mm	2650	2320	-		
Water Absortion (%)		0.45	6.49	-		
Friability Ratio (%)	0.1 - 2 mm	14.8	23.9	20.0	UNE 146404	
Sand Equivalent (%)	0 - 2 mm	87.7	75.28	68.73	UNE-EN 933-8	
Crushing Value (%)	10 – 12.5 mm	18.58	26.69	-	ISO 20290-3	
Los Angeles (%)	10 – 14 mm	20.0	34.72	-	UNE-EN 1097-2	

Table 2. Characterization of natural aggregate, mixed recycled aggregate and biomass bottom ash.

Natural aggregates present a density and absorption in line with other works [15] [16]. The density values of these works for medium and coarse natural aggregates (4 - 22mm) at 2.78g/cm³ and 2.65g/cm³ respectively and, with respect to their absorption, 1.91% and 1.8% respectively. For mixed recycled aggregate, Los Angeles coefficient and the ACV coefficient have values close to those of the natural aggregates, obtaining values from 14% to 24% for the angels and from 14% to 22% for the ACV [17]. Biomass bottom ash showed a high water absorption and a low bulk density, in accordance with others works [18] [19].

3. Experimental methods

3.1 Concrete manufacturing

In this study, six concrete mixes are included with different degrees of substitution: two conventional concrete dosages, one of them with fibres, two concrete mixes with MRA replacing aggregate, one of them with fibres and, lastly, two mixes which include Supplementary Cements Material (Eco-Hybrid Cement).



U (D]	CEM II	CEM	NA	NA	NA	MR	BB	WAT	SAT.	PLAS	SUPERPA	REL
[kg/m3]	A/L	EcHy	0/4	6/12	11/22	Α	Α	ER	WATER	TIF.	STIF.	w/c
	•	,	•	•	•							•
CTRL CEM II A/L	365	0	915	325	625	0	0	153	0	1.1	2.9	0.42
	265	~	720	215	445	45	0	150	25	1 2	4	0.42
25%WKA	305	0	730	215	415	2	0	153	25	1.2	4	0.42
CTRL CEM II A/L		•	045		<u></u>	•	•	450				
FIBRES	365	0	915	325	625	0	0	153	0	1.1	2.9	0.42
				407	450	90	•	450				
50%MRA FIBRES	365	0	591	137	156	4	0	153	55	1.9	4	0.42
EcHy al 25%	0	380	932	334	637	0	0	159	0	1.1	3.2	0.42
· ·												
27%MRA		200	500	4.60	161	48		450	20	4 5		0.42
3%BBA - EcHv	0	380	598	169	461	5	55	159	30	1.5	4	0.42
						2						

Table 3. Dosages of concrete mixes.

Saturation water is necessary for hydrate recycled aggregate, leaving available water for cement hydration. Two commercial additives were included in the concrete mixes.

3.2 Mechanical behaviour tests

To evaluate mechanical performance of concrete mixes, compressive strength was determined according to UNE-EN 12390-3, and flexural strength was determined according to UNE-EN 12390-5, two cylindrical specimens were tested per age for compression performance and two prismatic specimens were tested per age.

3.3 Dimensional changes

During the curing process, the dimensional changes that occurred in concrete mixes were measured. A micrometer precision comparator was used for these measurements, and the specimens tested were 4x4x28.5cm and measurements were taken at 2, 7, 14, 28, 56, 72 and 90 days. The mixes were arranged in two environments, in dry and wet chambers.

3.3 Open porosity and hardener density

Carried out under UNE 83980:2014 the hardened state density, water absorption coefficient and accessible porosity were determined for concrete mixes.



4. Results and Discussion

Following the traceability shown in the previous section, the results obtained for mechanical strength, dimensional changes and properties of hardened concrete are broken down.

4.1 Mechanical performance

In order to determine the mechanical behavior, the results obtained are shown in Figure 1



COMPRESSIVE PERFORMANCE

Figure 1: Mechanical performance of concrete mixes.

The results show that the application of fibres in the control concrete mixes increases the compressive strength by 6% to 8% and the flexural strength by 6% to 11%. When mixed recycled aggregate is replacing natural aggregate, it is observed that the resistance drops by 20% when we apply replacement of 25% of aggregate or 50% of aggregate while applying structural fibres, both in compression and flexural strengths. It should be noted that the mixes containing eco-hybrid cement increase their long-term resistance, exceeding the flexural resistance obtained with conventional concrete by 5% at one year of age. The mix in which eco-hybrid cement is applied and the aggregate is replaced by a combination of MRA and BBA, at early ages shows a reduction in compression and flexural strength of more than 25%, although, at 180



days and 365 days at compression and flexure respectively, the strengths only drop by 15% with respect to the conventional CEM II A/L concrete mix.

4.2 Dimensional changes

This section shows the dimensional changes undergone by the concrete mixes during curing in two types of environments, in a dry chamber and submerged.



Figure 2: Dimensional changes of concrete mixes.

In concrete mixes in the dry chamber, it can be seen, that the control mix reached a volume stability at 14 days, showing a shrinkage of 200 μ m/m, for the mixes with recycled materials, a shrinkage of 150 μ m/m or less was seen, and for concrete specimens subjected to water-immersed environment, the final shrinkage was less than 100 μ m/m. The only concrete mix that shows swelling is the mix containing BBA replacing 3% of the total aggregate, which shows a swelling of 122 μ m/m.

4.3 Open porosity and hardener density

Open porosity and hardener density were evaluated for all concrete mixes. The results are in Figure 3.



Figure 3. Open porosity and hardener density



The Density of hardened concrete is inversely proportional to the amount of accessible pores. The mixes with mixed recycled aggregate replacing natural aggregate are the ones with the highest accessible porosity and the lowest density. It should be noted that the mix with Eco-Hybrid cement, although it has a much lower density than the control mixes, with or without fibres, its accessible porosity is only slightly higher. This may be due to the fact that Eco-Hybrid cement is less dense than CEM II A/L cement.

5. Conclusions

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

- A similar pattern of mechanical behaviour was observed for conventional concrete mix and Eco-Hybrid concrete mix.
- The use of fibres produces a high mechanical performance, especially in flexion results.
- The use of BBA guarantees high long-term strength. A combination of BBA powder (included in Eco-Hybrid cement), BBA replacing natural sand, even with MRA replacing natural aggregate, has only a 15% drop in mechanical performance over the long term.
- The application of wastes such as mixed recycled aggregates and biomass bottom ash means that fresh mixes have to be adjusted (plus water and additive) to obtain the right consistency with the correct hydration of cement, without including an excessive amount of water that would create a large amount of pores, lower density and lower strength.

As a general conclusion, taking into account some parameters while mixing, and performing a correct pulverization of the residues to obtain properties similar to cement, it can be said that recycled concrete mixtures, with a high degree of replacement of conventional materials by recycled materials, are applicable to construction elements of civil engineering.

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MESOSCOPIC NUMERICAL SIMULATION OF CONCRETE

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Abstract

Concrete has been considered at mesoscopic scale as a heterogeneous material with three main phases: mortar, aggregates, and interfacial transition zone (ITZ). Aggregates are assumed to be spherical particles following the Fuller distribution, and only coarse aggregates, which account for 40% of the total volume of the concrete, are considered. The particles are randomly placed in the RVE by the "take and place" method, so that no overlapping occurs. Different shapes and sizes of reference volumes have been obtained numerically and will be used in compression tests in ANSYS. The stress-strain curves obtained in ANSYS are compared with those obtained in laboratory tests on specimens with identical grain size distribution, so that if the stress-strain curves are similar, one test can be substituted for another to draw conclusions on mechanical behaviour. In this way, the proposed numerical simulation method constitutes a methodology for compression tests commonly evaluated in the laboratory.

1. Introduction

Concrete is, together with steel, the construction material par excellence due to its capacity to adapt to any type of shape, withstand heavy loads and resist extreme environmental conditions. Being composed of different phases, it is a material whose behaviour and properties can vary at different scales, from the microscopic to the macroscopic [1,2].

At the microscopic level, concrete is composed of cement particles and water that combine to form the cement paste that surrounds the aggregates (sand and gravel). The microstructure of the paste is complex and can include porosities, micro-cracks and other defects that can affect its mechanical properties [3]. At the mesoscopic level, concrete is composed of three fundamental phases: the mortar (cement, water, and fine aggregate), the interfacial transition zone (ITZ) between the coarse aggregate and the mortar, and the coarse aggregates [4,5]. Finally, at the macroscopic level, it is considered as a single-phase material characterised mainly by its compressive strength and modulus of elasticity, as well as its flexural and tensile behaviour. In the design process with this material, these properties must be carefully controlled and verified to guarantee the safety and durability of the structures [6].



2. Materials and Methods

The heterogeneity of the internal structure of concrete makes its fracture behaviour non-linear, as it originates during the process of occurrence, propagation, accumulation, and fusion of micro-cracks. The behaviour of the material on a macroscopic scale is affected by various factors such as the geometry, distribution, and properties of its components, as well as the interactions between them. The micro-cracks that arise due to the internal heterogeneities of the material are responsible for the formation of the macroscopic cracks and the reduction of the stiffness of the material.

The fracture behaviour of concrete has been studied using various experimental and modelling techniques. The most common tests to evaluate its behaviour are compression, flexural, indirect tensile and shear tests.

Numerical models are essential tools for understanding and describing the properties of concrete, as well as for predicting its strength, the fracture pattern of the material and predicting its long-term performance and durability.

At the mesoscopic (millimetre) level, numerical models allow the behaviour of concrete to be analysed at the specimen level. The characteristics of the material are determined by the properties of its components and the relative arrangement between them: coarse aggregate, mortar, and interface. The use of numerical models at the mesoscopic level is of great interest for understanding the mechanical behaviour of concrete, including its fracture toughness and load-bearing capacity [7,8].

Mesoscopic numerical models are based on mechanics of materials and use finite element methods to simulate fracture in concrete under different loading conditions. In addition, these models allow analysing the effect of different parameters on concrete fracture, such as geometry, material strength and applied load rate. One of the main advantages of these models is that they provide a more complete view of fracture mechanisms and crack propagation, but they have some limitations such as the complexity of the implementation and the need for accurate experimental data to validate the results.

3. Experimental methods

In this case, a mesoscopic model has been developed in which concrete is composed of three phases: mortar, coarse aggregate, and transition zone.

A three-dimensional mesoscopic scale particle model of the concrete has been programmed in MatLab to obtain an .igs file (Initial Graphics Exchange Specification) for data exchange with Ansys. This file contains very complete information about the geometry of the model, i.e., shape, size, and position of the objects, representing the aggregates, mortar, and interface.

The programme works with some starting data, which are, among others: the dimensions of the RVE, which represents the test specimen used in the laboratory; the diameters of the aggregates, which are represented as spheres and their density; the percentage of mass of each aggregate size in relation to the total mass; the aggregate-cement ratio and the volume fractions of cement, aggregates, and water.

In a first phase, only two phases have been considered: mortar and aggregates, and two types of representative volumes: cube or cylinder, with the appropriate measurements of each of them being chosen. In this case, the cube has a side of 50 mm and the cylinder has a diameter of 25 mm and a height of 50 mm. The aggregate particles have diameters of 4, 6 and 8 mm and a percentage of 8%, 15% and 7% of the total



mass. The particle size distribution of the aggregates is of great importance for the characteristics of the concrete. The reference curve used is Fuller's parabola.

The filling of the volume is done randomly using the take and place method [9], placing the spheres from the largest to the smallest and considering the mass percentages of the data. To place a sphere, it must be considered that it is located completely within the domain, and anywhere in it, and that there must be no overlaps between them. A radius of influence of each sphere has been considered to avoid overlaps or contacts with the walls of the volume element. In all cases, the absence of pores has been considered.

Several test specimens have been simulated with different aggregate configurations, always complying with the volume fractions of the data.

Once the RVE has been generated with the spheres inside it, all the information on the centres and radii of the spheres and the size of the prism is transferred to Ansys, where the corresponding compression tests of the material will be carried out. It should be noted that Ansys must create a finite element model representing the geometry of the material and the applied load to calculate the stresses and strains of the specimen and determine crack propagation and fracture, so it depends on the quality and accuracy of the input data and its complexity.

In a second phase, the interfacial transition zone (ITZ) has been considered. The method followed to place the particles in the elemental volume is the same, but two concentric spheres were created where the volume between them is considered the interface. The consideration of the ITZ added complication to the Ansys finite element model, which cannot use elements smaller than a certain size (the size of the spherical crust is very small compared to the size of the finite elements used to discretise the spheres) and gives problems in the assembly of the two sizes of finite elements.

For this reason, and to reduce the number of finite elements, a prismatic RVE has been created, which corresponds to a quarter of the cubic RVE. In this volume, it is ensured that the spheres are complete, i.e., the volumes of the aggregates are fully preserved in the cube cut.

Figure 1 shows three RVEs corresponding to a cube of 50 mm edge, a cylinder of 20 mm diameter by 40 mm height and a prism of $25 \times 25 \times 50$ mm. The particles contained in the cube are 345, and those contained in the cylinder and prism are 68 and 87 respectively.



Figure 1: Different types of RVE used in tests.



4. Results and Discussion

The numerical method has been implemented with the Matlab program and the result is an .inp file whose appearance is shown in Figure 2, which will be transformed into igs format for Ansys. In this case, the reference volume generated was a prism of 25x25x50 mm, with aggregates of diameter 4, 6 and 8 mm. The first line of the file, after the preamble, contains information about the reference volume, which is centred on the reference origin, hence the negative coordinates in the x, y, and z directions:

block, -1.250000e+01, 1.250000e+01, -1.250000e+01, 1.250000e+01, -25, 25

The structure of the lines starting with *wplane* and *sph4* is then repeated as follows:

wplane, ,0 ,0 , z-coordinate, 1, 0, ph4, x-coordinate, y-coordinate, aggregate radius where the coordinates shown are the coordinates of the centre of each aggregate.

test00: Bloc de notas Archivo Edición Formato Ver Ayuda /clear,nostart /filname,test00.inp /title,Concrete mesostructure !Date: 21-Jun-2023 /prep7 !Inclusions block,-1.250000e+01,1.250000e+01,-1.250000e+01,1.250000e+01,-25,25 wplane,,0,0,-15.6314634301,1,0, sph4,6.1385020338,-2.7853668633,4.000000000 wplane,,0,0,5.8770755565,1,0, sph4,0.9000110368,-5.9557102098,4.000000000 wplane,,0,0,16.6525055440,1,0, sph4, -8.1849922478, -2.9174852930, 4.0000000000 wplane,,0,0,-8.6142694264,1,0, sph4, 3. 3617155569, 4. 9735628290, 4. 0000000000 wplane,,0,0,2.1196310235,1,0, sph4, -8.3148228495, 4.6818872984, 4.000000000 wplane,,0,0,-8.2069842220,1,0, sph4, -7.9174498793, 5.7621123422, 4.000000000 wplane,,0,0,6.9099816375,1,0,

Figure 2: Detail of the .inp file for a prismatic specimen with a base of 25 mm and a height of 50 mm.

5. Conclusions

The proposed model will serve as a basis for establishing a methodology to numerically simulate the compression tests commonly performed in the laboratory.

- It will provide detailed information on the behaviour of concrete at mesoscopic scale, which can help to understand its deformation and fracture mechanisms and lead to better design with this material.

- They are an inexpensive and fast alternative to evaluate concrete behaviour and save some of the drawbacks of experimental methods, although they can by no means be a substitute.



- They help to investigate how specific properties of other materials affect the behaviour of concrete, such as the addition of fibres.

- They can identify areas where the material is more prone to failure.

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MECHANICAL BEHAVIOUR OF SELF-COMPACTING CONCRETE REINFORCED WITH ABACA FIBERS.

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Abstract

The interest in using natural fibers as reinforcement in concrete has gradually grown in response to the need for environmentally friendly building materials. These fibers exhibit additional benefits such as light weight and strong tensile strength in addition to being renewable, affordable, and having a superior life cycle. This work aims to evaluate the influence of Abaca Fibers (AF) in self-compacting concrete, by designing an optimum dosage and analysing its mechanical behaviour. Respective tests were carried out to determine the parameters of concrete, both in fresh and hardened state. Related to the reference concrete, manufactured with the same characteristics, AF obtained suitable results in terms of compressive and flexural strength, fitting within the permissible range of self-compacting concrete.

1. Introduction

Fiber reinforced concrete is a composite material that improves structural integrity and strength by incorporating fibrous material. The addition of fibers, enhance concrete's mechanical properties, contributing to control the cracks and crack growth [1]. Natural fibers have been used in construction since the beginning of human civilization, by mixing them with earth and cementitious materials, to improve the mechanical strength of building materials [2]. Currently the incorporation natural-origin resources in the construction sector has increased, due to growing environmental concerns [3]. The advantages of using plant fibers as an alternative are their light weight, low cost, biodegradability, and high specific stiffness [4].

Abaca fiber is acquired from the plant commonly known as Manila hemp (*Musa textilis*), abundant in tropical countries like Philippines, these fibers possess high tensile and flexural strength [5]. Poor dispersion in cementitious matrix could be mentioned as the most critical limitation for natural fibers in concrete [6]. However recent studies have analysed different treatments to increase the stability of this reinforcement in the matrix bond, giving promising results [7]. Many fibers have been used to enhance the properties of concrete, but most of them have been synthetic [8]. Although there are exceptional



studies of abaca fibers in concrete, in general terms they are employed in mortars [9]. This work aims to study an ideal dosage for abaca reinforced concrete and evaluate its mechanical behaviour.

2. Materials

2.1 Cement

The cement used was Portland Cement, type CEM I 42.5 R-SR 3 [10], provided by "Cementos Portland Valderrivas, S.A." located in Alcala de Guadaira, Seville, Spain.

2.2 Filler

The filler applied has a limestone-dolomitic nature, with a density of 2.830 kg/m³, crushed material supplied by "Triturados Puerto Blanco", company placed in Huetor-Santillan, Granada, Spain.

2.3 Natural Aggregates

Natural Sand (NS) practically free of fines, 0/4 mm size. Natural Coarse Gravel (NCG) and Natural Medium Gravel (NMG), particle size of 8/16 mm and 4/8 mm respectively. All with limestone-dolomitic nature, provided by "El Rayo" quarry located in Loja, Granada, Spain.

2.4 Abaca Fibers

Particularly, these fibers were imported from Ecuador, second largest supplier worldwide after Philippines [11], cut to a length of 30 mm. According to previous literature, before being added to the mixture, the AF received a chemical treatment of NaOH to increase the degree of homogeneity between the cementitious matrix and the fibers [12].

3. Experimental methods

3.1 Concrete manufacturing

Seeking a uniform distribution of abaca fibers in the mixture, a self-compacting concrete was designed for this study, specifically of type HA-30 / AC / 16 / XC3 according to the Structural Code. This code doesn't include a minimum quantity of fibers for structural concrete, however, recommends not to use less than



0.25 % in concrete volume [13]. Therefore, the first batch manufactured, designated as Abaca Fibers Self-Compacting Concrete (AF SCC) included 2.5 kg/m³ of fibers, 0.55 of water/cement ratio and a superplasticizer as an additive, MasterEase 3530. On the other hand, to have a direct comparison, Reference Self-Compacting Concrete (RF SCC) was casted, with the same proportions, excluding the abaca fibers.

3.2 Workability of the fresh concrete

Self-compactability tests were developed to determine the workability of concrete in fresh condition, according to the Structural Code [13] and the respective standard for each test:

- a) Slump-Flow: measurement of concrete's flow extension (SF) [14].
- b) V-Funnel: time (tv) to evaluate concrete's vertical flow under its own weight [15].
- c) J-Ring: difference in height (PJ), to measure concrete's flow through narrow openings [16].
- d) L-Box: ratio between horizontal and vertical heights (PL), for concrete's flow capacity [17].

3.3 Mechanical behaviour tests

Concrete elements were unmoulded 24 h after casting, maintaining the given requirements for making and curing specimens for strength tests [18]. The tests of hardened concrete were made as follows.

3.3.1 Compressive strength

Cubic samples (100 x 100 mm) were used to determine compressive strength in each type of concrete, tested at 7, 14 and 28 days respectively [19].

3.3.2 Flexural strength

Prismatic samples (100 x 100 x 400 mm) were tested at 28 days, to analyse the flexural behaviour of AF SCC and RF SCC [20].

4. Results and Discussion

4.1 Dosage

The ideal dosage was accomplished after a series of mixing tests to adjust the self-compacting parameters. Dosages are shown in Table 1, as it can be noticed, the concrete mixtures, discarding the fibers, were made with the same quantity of materials.



Table 1: Dosages of the concrete mixtures								
	DOSAGE (kg/m ³)							
	Water	Cement	Filler	NS	NCG	NMG	SP	AF
AF SCC	165	300	309	680	536	536	6.6	2.5
RF SCC	165	300	309	680	536	536	6.6	-

lacadas of the concrete mixtures

4.2 Self-compactability

In line with the parameters of the Structural Code [13], both concretes fulfil the permissible range for obtaining the self-compactability condition, as it is shown in Table 2.

	-	•	-				
	MEASURED PARAMETER						
	Slump-Flow	V-Funnel	J-Ring	L-Box			
	SF (mm)	tv (s)	PJ (mm)	PL			
AF SCC	770	18.2	9.5	0.8			
RF SCC	760	17.1	9.0	1.0			
Permissible Range	550-850	≤ 25 s	≤ 10 mm	≥ 0.80			

Table 2: Results of self-compactability tests according to Structural Code

4.3 **Mechanical behaviour**

Regarding compressive tests, Figure 1 shows the values of the resistance obtained for each mix, according to their respective age. Even that the results were similar, as expected, RF SCC showed slightly superior compressive strength; however, AF SCC presented a higher increase in time.



Figure 1: Compressive strength resistance related to age.



On the other hand, Table 3 shows the results of flexural strength at 28 days for each mix. The values obtained demonstrate that AF enhanced concrete's resistance, in line with expectations.

	FLEXURAL SRTENGTH					
		Load	Resistance			
	Age (days)	(kN)	(MPa)			
AF SCC	28	18.75	8.33			
RF SCC	28	17.48	7.76			

Table 3: Flexural strength test at 28 days.

5. Conclusions

Based on the results attained, we present the following specific conclusions:

- With the optimal dosage, self-compactability parameters were achieved in both concretes.
- AF SCC had lower compressive strength, compared to RF SCC, but higher increase in time.
- As anticipated, AF improved flexural strength, providing ductility to the elements tested.

In general, abaca fibers presented favourable outcomes in terms of mechanical behaviour. The research shall move forward with durability testing, to further the understanding of these fibers as a reinforcement to the concrete mixture.

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EVALUATION OF THE SELF-HEALING CAPACITY OF CONCRETE CONTAINING INDUSTRIAL WASTES USING THE WATER PERMEABILITY TEST

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Abstract

Self-healing is the ability of a material to recover its properties after suffering some damage, usually cracks. In the last years, various strategies have been studied to promote self-healing in concrete, being the employment of porous aggregates as water reservoirs for the internal curing of concrete or the incorporation of supplementary cementitious materials some of them. This research work studies the self-healing capacity of conventional self-compacting concrete by incorporating metakaolin and biomass ash as filler and granular coal combustion products as aggregates, both these last ones, residues from industrial processes.

1. Introduction and objectives

Reinforced concrete elements often work under cracking conditions. These cracks can affect the durability of the structure by providing a preferential way of entry for aggressive agents [1]. It is known that concrete has an inherent healing potential called autogenous healing, which can take place through two main mechanisms: i) the hydration of un-hydrated cement particles [2] and ii) the precipitation of calcium carbonate [3,4]. The presence of water is vital for autogenous healing and this can be supplied by using internal curing agents. The healing efficiency of some supplementary cementitious materials with pozzolanic activity has also been proved in various research works. Testing methods to quantify the healing efficiency are numerous being the water permeability test performed under cracked conditions one of the most employed in the literature [5,6].

Recent studies have investigated the use of coal bottom ash (CBA) as aggregates in concrete. CBA shows a high capacity to absorb water (up to 35%) [7]. This aggregate, when introduced into the concrete mix, can slowly provide water to the cement paste promoting self-healing through sustained hydration and precipitation of calcium carbonate [8]. On the other hand, due to the use of forest matter as fuel in electricity production, the production of different biomass ashes (BA) is increasing [9]. Some studies have suggested their beneficial use as new supplementary cementitious materials (SCMs) [10]. Finally, metakaolin (MK) is one of the most promising SCMs with a pozzolanic activity that can also contribute to the self-healing capacity.



This study aims to analyse the self-healing capability of a concrete incorporating 25% BA and 15% MK as a binder together with 30% CBA as fine aggregate (< 4 mm) using the water permeability test as an indicator of crack sealing.

2. Materials and methods

2.1 Materials and mixes

The materials used in this study include CEM I 52.5 N (C) metakaolin (MK) biomass ash (BA) as powder materials (Table 1). The conventional aggregates are a 0/4 crushed sand (NS) and a crushed gravel (NG) with a maximum size of 12 mm. The natural sand was partially replaced (30%) by coal bottom ash (CBA). The CBA was produced during the combustion of coal at a power station. The main physical properties of these materials are shown in Table 1

Binders	С	MK	BA
Density (g/cm ³)	3.04	2.55	2.68
Specific surface area BET (m ² /g)	1.36	4.25	0.63
D ₁₀ (µm)	4.91	4.18	36.87
D ₅₀ (µm)	23.69	20.96	90.07
D ₉₀ (µm)	49.77	112.17	186.27
Aggregates	NS	СВА	NG
Saturated-surface-dry density (kg/m ³)	2.72	1.62	2.81
Water absorption 24 h (%)	1.05	36.7	0.65
Flakiness index (wt%)	-	-	17
Los Angeles coeficient (wt%)	-	-	18

Table 1: Physical properties of raw materials.

With these raw materials two concrete mixes were designed (Table 1): i) a baseline concrete with Portland cement and natural sand (100C) and ii) an eco-concrete with 25% BA and 15% MK as a binder in combination with 30% of CBA replacing the natural sand (60C25B15MK-30CBA). A 0.6% of superplasticizer (SP) (considering the active powders) was used to improve workability. All aggregates were used moist conditions pre-soaking them, before mixing, with the water needed to get the 80% of their water absorption.



	С	MK	BA	NS	CBA	NG	Water	W/C
100C	189.93	-	-	300.00	-	300.00	209.00	1.10
60C25BA15M-30CBA	114.90	28.51	47.52	210.00	90.00	300.00	209.00	1.10

Table 1: Concrete mix design by volume (I/m³).

2.2 Assessment of self-healing capacity

Three testing samples were made using cylindrical specimens ($\emptyset 100x200 \text{ mm}$). They were demoulded at 24 hours and at three days they were cut into four disks of $\emptyset 100x40 \text{ mm}$. During all the testing procedure the curing process was developed by immersion the samples in tap water at 20°C ±2°C.

At the age of 7 days, the samples were pre-cracked by a splitting test developed at a cracking opening rate of 0.2 μ m/s up to a crack opening value of 300 μ m. Crack width was controlled by means of a Linear Variable Differential Transformers (LVDTs) and the generated crack was then mapped with a digital microscope DinoLite®. The crack width was measured at eight equidistant points along the crack length on the top and bottom faces of the sample. The average crack width was thus calculated as the average of the 16 measurements.

Just after pre-cracking, the permeability test was performed introducing over the cracked sample a constant water height of 450 mm using plastic tubes of \emptyset 100 mm inserted in a permeability cell. The tests were maintained for 1 h and the amount of water that flows through the crack was weighed every 5-min by electronic balances. The water flow rate in mL/(hora) was then obtained.

After that, all samples were maintained in tap water at 20°C for 21 days to promote the self-healing. Then, at the age of 28 days, the measurement of the crack width and the permeability test were repeated.

The self-healing capacity was then calculated considering the two following parameters:

The Index of Crack Sealing (ICS), Eq.1.

$$ICS = (1 - \frac{wi}{w_{t0}}) \times 100 \tag{Eq-1}$$

Where w_{to} and w_i are the crack widths at 7 days and at the end of the healing period, respectively. The Index of Permeability Healing (IPH), Eq.2.

$$IPH = (1 - \frac{K_i}{K_{t0}}) \times 100 \tag{Eq-2}$$

Where K_{io} and K_i are the water flow rate at 7 days and at the end of the healing period, respectively.

3. Results and Discussion

Figure 1 shows the ICS and the IPH vs the initial crack width of both mixes. According to these indexes, both mixes show a significant healing capacity after the water curing period. In addition, it is confirmed that the sealing kinetics depends on the initial crack opening (the indexes decrease when the initial crack



width rises). This trend was also observed by Cuenca et al. [6] on pre-cracked and geothermal water cured concrete.

Comparing the behaviour of the two mixes when the initial crack width is similar, it seems that the conventional concrete presents higher index than the eco-concrete, probably due to two main factors: i) a lower amount of cement available to react and ii) a lower degree of hydration compared to the reference mix.



Figure 1: ICS vs. initial crack width (a), IPH vs. initial crack width, (b)

According to the results shown in figures, a good correlation between the IPH and the ICS was observed. This means that both indices are suitable to define the concrete healing capacity.

4. Conclusions

The following conclusions can be drawn from the analysis of the results:

- Crack sealing was slightly more effective in the conventional mix than in the eco-concrete with BA, MK and CBA. When the initial crack width is between 110 and 170 µm both the Index of Crack Sealing and the Index of Permeability Healing were around a 20% lower in the eco-concrete than in the conventional mix.
- The healing capacity of both mixes decreases when the initial crack width rises which means that autogenous healing is more effective when the crack width is low.
- Both testing parameters, the ISC and IPH, show a very good relationship, indicating that they can be used to measure the healing capacity of the concretes.

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CONSTRUCTION OF A LORRY PARKING AREA AT THE SIDERURGICA SEVILLANA COMPANY BY REUSING STEEL SLAG FROM A LANDFILL SITE

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Abstract

This study presents the work currently being carried out to modernise the heavy vehicle car parks of the company SIDERÚRGICA SEVILLANA. The car parks have a surface area of more than 18000 m2 and are located on a former iron and steel slag dump.

The possibility of reusing the slag deposited in the landfill for soil stabilisation using HRB and soil treated with cement, offers great advantages from a mechanical, environmental, and economic point of view.

1. Introduction

Studies for the integrated utilisation of electric furnace slag are not new. The annual production of steel slag in Europe is 21 million tonnes [1]. Currently, steel slag can be recycled for in-house metallurgical purposes [2] or used in road construction [3 - 6], cement and concrete [7], bituminous mixtures [8], and soil improvement [9].

Due to the high demand for natural resources in the construction sector, today's society has a growing interest in finding alternative materials to replace the use of raw materials from nature. Therefore, extensive studies have been carried out to explore the possibility of using steel slag as alternative materials, reducing CO2 emissions and the total cost of materials used [10]

The use of steel aggregates in the execution of civil works, especially roads, is a relatively recent development in Spain, with the most frequent destination of steel slag being landfill disposal. The separate treatment of black slag from electric arc furnaces (EAFS) and white slag from refining or ladle furnaces (LFS) has allowed the former to be used as aggregate for construction in different uses, either as filler in sub-base and base layers, or as aggregate incorporated into the bituminous concrete layers that make up the road surface section. In the case of white slag, it has been used mainly as a by-product in the manufacture of cement. However, there are still large areas of waste that can be reused.



2. Research Design Designed solution. Justification

In an extensive process of modernisation of its facilities, Siderúrgica Sevillana company included a modification of the location of the scales and its control building, modifying the entry point to the factory and the distribution of traffic in it, as well as a profound improvement of the esplanade of the current car parks.

Within the context of a circular economy, and coinciding with the philosophy of Siderúrgica Sevillana, the possibility of studying the reuse of the iron and steel slag deposited there many years ago, as well as the iron and steel aggregates that had been used in the different extensions carried out over the years, was put to the Management. The possibility of reusing the landfill site offered great advantages from an environmental and economic point of view (minimisation of excavation volumes and transport to the landfill site if necessary, reuse of materials at the end of their useful life from other industries and a reduction in the consumption of natural resources), resulting in a much more sustainable solution from all environmental and economic points of view, as well as allowing a reduction in the time required for execution.

To technically verify this alternative, and once the new configuration of the car park and weighbridge complex had been designed (figure 1), a geotechnical reconnaissance and testing campaign was designed to determine the composition of the materials that make up the current esplanade, to try to establish their stratification and determine their bearing capacity. As well as the possibility of reusing the materials of iron and steel origin deposited there.



Figure 1: Situation prior to the works

3. Designed solution. Justification

The conclusions drawn from the geotechnical campaign were as follows:

- Soil very heterogeneous in its composition and in the arrangement of materials.
- Slag deposits very variable in thickness and extension.
- Slag recoverable for valorisation
- Acceptable previous support capacity of the existing terrain.



With these conditioning factors, solutions were proposed based on stabilised soils and materials treated with cement, after checking to ensure that they were suitable for both treatments, as well as seeking asphalt mixtures that offered high performance against tangential stresses and great flexibility, due to possible settlement of the supporting soil and risk of cracking. The asphalt mixes had to be tested to ensure that they were suitable for both treatments.

4. Experimental methods and Result

4.1 Hydraulic Road Binder (HRB)- stabilised soil

A soil stabilisation study was carried out (mixture of natural soils and steel slag) with HRB, using the binder i. tech STABILE ORIGINAL. Subsequently, the corresponding working formulas and workability period were obtained. Two working formulas were developed in order to pre-characterise the two predominant soil types. he results of compressive strength are shown in table 1.

	Specimen 1	Specimen 2	Specimen 3	MEDIA	-	
Strength 3 days (MPa)	1.19	2.78	2.3	2.04	-	
Strength 7 days (MPa)	2.11	3.27	2.3	2.22		
Density (gr/cm ³)	1.99	2.16	1.99	2.03		
Moisture (%)	11.88	13.37	12.77	8.97		

Table 1: Compressive strength (MPa) Phase 1

4.2 Soil Cement

A 25 cm thick layer was designed, executed in situ by dry method. Untreated slag and iron and steel aggregates were used as filler material, after treatment at the recovery plant. For this purpose, a classification of the materials was carried out during the excavation, and a during excavation and stockpiled for subsequent treatment at the plant. The material thus treated conformed to the SC40 grain size range, and all the tests on the suitability of the material for use in the manufacture of soil-cement yielded satisfactory results.

Prior to the completion of compaction, the layer was pre-cracked to a depth of approximately 16 centimetres (2/3) of the thickness of the layer, in a 4 x 4 metre mesh.

Tests were carried out on the finished unit to determine the density "in situ" including humidity by the radioactive isotope method (soils) UNE 103900:2013 and simple compression test (soil-cement) UNE EN 13286-41:2003. The results of compressive strength are shown in table 2.



	Specimen 1	Specimen 2	Specimen 3	MEDIA
Strength 3 days (MPa)	3.8	1.8	2.1	2.6
Strength 7 days (MPa)	4.1	2.8	2.6	3.2
Density (gr/cm ³)	2.43	2.34	2.35	2.4
Moisture (%)	9.2	10.96	11.2	10.5

Table 2: Compressive strength (MPa). Phase 1

All the simple compression tests gave satisfactory values, the average value of the tests being 3.16 MPa at 7 days. mean value of the tests was 3.16 MPa at 7 days.

5. Conclusions

After analysing the results of this work:

- No vertical deformation of any kind has been observed in any area of the esplanade, nor is there any detachment of aggregate in the surface layer.

- Reduction of the carbon footprint due to the reduction of the transport distance (aggregate treatment plant just 900 metres from the site).

- Reduced landfill requirements. Minimisation of the use of natural material. Improvement in site execution times.

In general, a very advantageous execution from an environmental and economic point of view, with excellent technical performance.

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ESTUDIO DEL COMPORTAMEINTO DE CENIZAS PROCENDENTES DE CENTRALES ELÉCTRICAS DE BIOMASA EN LA INDUSTRIA CEMENTERA

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Abstract

In recent years, research applied to materials used in construction has focused on developing environmentally friendly binders with a low carbon footprint, which also incorporate industrial or agroindustrial waste as raw materials to promote the Circular Economy. Portland cement production is an energy-intensive activity (around 30% of production costs) and generates between 0.7 and 1.2 tonnes of CO2 per tonne of cement produced [1], making it a sector that generates enormous quantities of greenhouse gases into the atmosphere, accounting for 8% of global carbon dioxide emissions [2].

The aim of this work is therefore to obtain hybrid cements consisting of a mixture of Portland cement (in a maximum proportion of 40%), biomass ashes and solid chemical activators capable of stimulating the reactivity of the mixtures.

The use of biomass ashes in large quantities is one of the major challenges facing the building materials sector to make a positive contribution to the environment.

The mechanical properties, compressive strength and flexural strength of the materials produced were studied.

1. Introduction

Climate change is a fact of life and finding feasible strategies to reduce greenhouse gas emissions from industrial processes, while maintaining economic growth, is an immediate challenge. The Portland cement (PC) and concrete industries contribute $\Box 8$ % of total man-made CO2 emissions; and if that were not enough, PC production is expected to increase in the near future to maintain adequate living standards everywhere. In short, there is an urgent need to work on strategies for the production of sustainable building materials that also keep mechanical performance and durability requirements at a good level.

As a current figure, 30% of the pomace produced in Andalusia is destined for combustion to generate electricity. This gives an idea of the amount of ash generated during the combustion of by-products



originating from the olive grove sector, it should also be noted that a large part of the olive grove is collected for combustion (olive pruning, trunks). In addition, there are other biomass wastes that are also of interest due to their production volume. For example, for every tonne of rice, 200 kilos of husk are produced which, after burning, generates 40 kilos of ash. The same applies to almond shells, cotton waste and beer bagasse.

2. Properties of Materials

2.1 Cement

The reference cement used was CEM-I 52.5R provided by Cementos Cruz and different biomass ashes from different energy cogeneration plants distributed throughout Spain, as can be seen in Figure 1. To characterise the ashes, the equipment provided by Cementos Cruz was used: X Ray Diffraction Bruker; Fluorescence X Ray Bruker; Laser Diffractometer Mastersizer 3000.

2.2 Mix proportions

Table 1 shows the proportions followed for this study:

95% CEM1 + 5% BFA(AEAnd)
90% CEM1 + 10% BFA(AEAnd)
85% CEM1 + 15% BA(AEAnd)
80% CEM1 + 20% BA(AEAnd)*
70% CEM1 + 30% BA(AEAnd)
60% CEM1 + 40% BA(AEAnd)
95% CEM1 + 5% BFA(VAL)
90% CEM1 + 10% BFA(VAL)
80% CEM1 + 20% BFA(VAL)
70% CEM1 + 30% BFA(VAL)
60% CEM1 + 40% BFA(VAL)
95% CEM1 + 5% BBA(VAL)
90% CEM1 + 10% BBA(VAL)
80% CEM1 + 20% BBA(VAL)
70% CEM1 + 30% BBA(VAL)
60% CEM1 + 40% BBA(VAL)
95% CEM1 + 5% BFA(HRM)
90% CEM1 + 10% BFA(HRM)

Table 13: Mix Proportions



80% CEM1 + 2 0% BFA(HRM)
70% CEM1 + 30% BFA(HRM)
60% CEM1 + 40% BFA(HRM)
95% CEM1 + 5% BFA(LOMA)
90% CEM1 + 10% BFA(LOMA)
80% CEM1 + 20% BFA(LOMA)
70% CEM1 + 30% BFA(LOMA)
60% CEM1 + 40% BFA(LOMA)
95% CEM1 + 5% BBA(LOMA)
90% CEM1 + 10% BBA(LOMA)
80% CEM1 + 20% BBA(LOMA)
70% CEM1 + 30% BBA(LOMA)
60% CEM1 + 40% BBA(LOMA)

 Table 2: Chemical composition obtained by X-ray fluorescence (XRF) of the biomass ashes used in the work.

 LFA: La Loma fly ash, LBA: La Loma bottom ash, AEFA: Aldebarán energía fly ash, AEBA: Aldebarán Energía bottom ash, VFA: Valoriza fly ash, VBA:Valoriza bottom ash, HRM: Herba rice mills.

Oxide	LFA	LBA	AEFA	AEBA	VFA	VBA	HRM
SiO ₂	12,39	19,15	19,19	37,17	26,01	35,92	70,19
Al ₂ O ₃	2,68	4,00	3,67	5,65	6,945	7,36	0,06
Fe ₂ O ₃	1,05	1,77	1,55	2,62	3,58	4,01	0,301
CaO	5,78	9,67	25,63	25,56	19,28	3,28	1,22
MgO	3,37	4,51	4,83	3,89	3,65	25,11	1,12
K ₂ O	31,67	24,29	19,9	10,2	12,08	6,9	3,53
Na ₂ O	0,66	0,99	0,546	0,36	0,53	0,46	0,25
P2O5	3,74	5,43	3,13	2,1	1,74	1,14	2,05
SO ₃	4,92	1,19	3,11	0,76	4,14	0,42	1,01
TiO ₂	0,15	0,24	0,194	0,33	0,53	0,54	0,02
ZnO	0	0	0,07	0,01	0	0	0
SrO	0	0	0,07	0,06	0	0	0
MnO	0	0	0,06	0,06	0	0	0,13
LOI	33,569	28,743	16,21	11	21,524	14,868	19,29



3. Experimental methods

The aim of this study is to quantify the reactivity of biomass ash as a replacement for clinker in the creation of hybrid cements, to study the strength behaviour of these cements and to check the feasibility of incorporating biomass ash in the cement industry.

3.2 Mechanical properties

At 7, 28 and 90 days, the flexural strength of RFS mortar mixes was evaluated following UNE 196-1 using standardized mortar specimens measuring 40 mm \times 160 mm \times 160 mm. Subsequently, the two halves of the mortar were tested for compressive strength using the same standard.

4. Results and Discussion

Figure 1 shows the geographical distribution of the locations of the ash generation plants analysed.



Figure 1: Distribución geográfica de las plantas generadoras de cenizas de biomasa analizadas.

4.2 Mechanical properties

Figures 2, 3 and 4 below show the results of compressive strengths of standardised mortars at 2, 7 and 28 days comparing the different additions of each type of biomass ash (fly ash and bottom ash) and taking CEM-I 52.5R cement as a reference. It can be seen that the best mechanical strengths are obtained for hybrid cements formulated with the lower ash proportions, i.e. for additions of 10 and 20 % by weight of ash, in general. In particular, the best results are obtained for Aldebaran fly ash with values of 59 and 57



MPa at 28 days for 10 and 20% additions, and the worst for Herba Rice Mills rice husk ash, reaching values of 55 and 49 MPa, which although being the lowest of all the ashes used, are very good results. This may be due to the chemical composition of the ashes as can be seen in Table 1. Thus, the AEFA ashes (Aldebarán Energía fly ash) have a comparatively higher calcium content than the rest of the series, and the Herba Rice Mills ashes have the lowest calcium content, as the rest of the interesting components such as silica or alumina do not show any major differences.



Figure 2: Compresive Strengh in 2 days with different biomass ashes







Figure 3: Compressive strength in 7 days with different biomass ashes



Figure 4: Compressive strength in 28 days with different biomass ashes



5. Conclusions

The following results are obtained from the results obtained:

- The addition of up to 20% in some biomass ashes only reduces their mechanical properties by 10%, which favours the replacement of clinker by these ashes.
- The amount of ashes produced annually by the different companies has been increasing in recent years, which makes these materials viable in cement additions.

6. Acknowledgements

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A NEW POROUS AND PHOTOCATALYTIC GEOPOLYMER COMPOSITE FOR DEGRADATION OF RHODAMINE B

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Abstract

In this work, we studied the incorporation of a TiO₂ semiconductor in the geopolymer matrix as catalytic materials. We present the synthesis of a novel TiO2/geopolymer nanocomposite as an effective ecological catalyst with highly efficient photocatalytic properties under UV light irradiation. The Photocatalytic geopolymers were prepared by simple method, the TiO₂ nanoparticles were successfully loaded into the geopolymer matrix by geopolymerization reaction. Furthermore, the results indicate that the prepared photocatalytic geopolymer matrix provides an easily recyclable and reusable support for TiO₂ nanoparticles in the photocatalytic process that efficiently separated the photogenerated charges. Finally, the physicochemical and morphological composition of samples was characterized by several techniques, namely X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV–Vis Diffuse Reflectance Spectroscopy (DRS). Thermal Analysis (TGA/TDA), N2 Adsorption/Desorption Isotherms Analysis (BET and BJH methods), Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Analysis (EDAX).

Keywords: Geopolymer, alkaline activation solution, wastewater treatment, Photocatalysis, Rhodamine B.



1. Introduction

Photocatalytic geopolymers have emerged as a promising technology for the degradation of dyes in wastewater treatment. Dyes are widely used in various industries, including textile, printing, and paper manufacturing, but their disposal into water bodies poses significant environmental challenges. Conventional methods of dye removal, such as adsorption or chemical precipitation, have limitations in terms of efficiency and cost-effectiveness. Photocatalytic geopolymers offer a sustainable and effective alternative for the degradation of dyes through the synergy of photocatalysis and geopolymerization.

Geopolymers are inorganic polymers formed by the reaction of aluminosilicate materials with alkaline activators. They possess excellent mechanical properties, chemical stability, and fire resistance, making them suitable for various applications. In recent years, researchers have explored the incorporation of photocatalytic materials, such as titanium dioxide (TiO₂), zinc oxide (ZnO), or other metal oxides, into geopolymer matrices to enhance their photocatalytic properties.

2. Properties of Materials

Photocatalytic activity: Photocatalytic geopolymers exhibit high photocatalytic activity due to the incorporation of photocatalytic materials, such as titanium dioxide (TiO2) or zinc oxide (ZnO), within the geopolymer matrix. These materials can generate reactive oxygen species (ROS) when exposed to UV or visible light, which can effectively degrade organic dyes.

Stability: Geopolymers are known for their excellent chemical stability. The geopolymer matrix provides a stable structure that can withstand harsh environmental conditions, including exposure to acidic or alkaline solutions, high temperatures, and mechanical stress. This stability ensures the longevity and effectiveness of the photocatalytic process.

Porosity: Photocatalytic geopolymers possess a porous structure that enhances the accessibility of dye molecules to the photocatalytic active sites. The porous nature of the geopolymer matrix facilitates the diffusion of the dye molecules into the material, maximizing the contact area with the photocatalyst and promoting efficient dye degradation.

Immobilization of photocatalyst: One of the key advantages of photocatalytic geopolymers is the immobilization of the photocatalyst within the geopolymer matrix. This immobilization prevents the leaching of the photocatalyst into the treated water, minimizing environmental contamination. It also ensures the long-term stability and reusability of the photocatalytic material.

Cost-effectiveness: Photocatalytic geopolymers can be synthesized using low-cost raw materials, such as fly ash, slag, or metakaolin, which are abundant industrial by-products. The utilization of these readily available materials reduces the production cost of the photocatalytic geopolymers, making them a cost-effective solution for dye degradation in wastewater treatment.



3. Mix proportions

The protocol for preparing photocatalytic geopolymers for dye degradation involves several steps. Firstly, the geopolymer mixture is prepared by mixing the aluminosilicate source with an alkaline activator. The desired amount of photocatalytic material is then incorporated into the mixture and thoroughly mixed to ensure even distribution. Next, the geopolymer mixture is molded into the desired shapes and sizes. The geopolymers are then cured at room temperature for a period of 24 to 48 hours to facilitate geopolymerization and achieve sufficient strength. After curing, the geopolymers are dried in a well-ventilated area for several days to a week. Subsequently, the photocatalytic activity is tested by exposing the geopolymers to UV or visible light and immersing them in a dye solution. The degradation of the dye is analyzed over a specific duration to evaluate the efficiency of the photocatalytic process. Further optimization and testing can be conducted by modifying the geopolymer composition or parameters to enhance the photocatalytic performance.

4. Experimental methods



The irradiation protocol for photocatalytic geopolymers can be summarized in the figure below:



5. Results and Discussion

5.1.XRD analysis

The XRD patterns of the photocatalytic geopolymers samples synthesized for photocatalytic purposes show the presence of TiO_2 nanoparticle peaks (26 and 38°), signifying the incorporation of TiO_2 nanoparticles into the geopolymer structure. Moreover, an amorphous structure in a wide range positioned at about 27 °C is formed [1].



Figure 1: X-rays of ADS-800 and photocatalytic geopolymers.

5.2.Photocatalytic performance: Photodegradation of Rhodamine B

In order to investigate the impact of photolysis on the photocatalytic characteristics of the fabricated samples, a test was carried out under UV illumination and without any photocatalyst (photolysis) was performed as shown in Fig. 12. The results showed that photolysis alone led to a degradation efficiency of less than 2%. Therefore, it can be inferred that the degradation of organic pollutants was not primarily caused by photolysis. The adsorption of RhB by photocatalytic geopolymers GPT1 and GPT2 in the dark was around 31% and 38% respectively after 60 minutes, which could be attributed to the presence of surface pores and functional groups in the synthesized geopolymers. This adsorption behavior has been previously reported in our published work [2].





6. Conclusions

We have successfully created a photocatalytic geopolymer through a simple method in this study. Our research focused on examining the structural, porous, optical, and photocatalytic properties of the geopolymer. By incorporating TiO₂, we were able to develop mesoporous geopolymer materials effectively. During the geopolymerization reaction, TiO2 nanoparticles were uniformly dispersed, significantly enhancing the photocatalytic capabilities of the geopolymer. Various analyses, including XRD, BET, TGA/DTA, and SEM, revealed that the introduction of TiO2 particles led to a reduction in the number of pores and voids, resulting in denser geopolymer structures. Moreover, the integration of titanium species into the geopolymer network structure modified its morphology. These photocatalytic geopolymers exhibited remarkable thermal stability at high temperatures, enduring up to 1000°C. Furthermore, we discovered that our photocatalytic geopolymer samples, named GPT1 and GPT2, effectively decompose rhodamine B (RhB) by harnessing the synergistic effects of adsorption and photocatalysis.

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