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Microstructure, Durability and Mechanical Properties of Mortars Prepared Using Ternary Binders with Addition of Slag, Fly Ash and Limestone †

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Abstract: Nowadays, in order to reach a more sustainable cement industry, several strategies have been developed. One of them is to increase the use of eco-friendly cements with lower content of clinker, replacing it by additions. Among them, the characterization of the performance of mortars and concretes prepared using cements with ternary binders, which incorporate two additions, are now an important field of study. In this research, the microstructure, durability-related properties and mechanical strength of mortars prepared using three ternary binders with incorporation of ground granulated blast furnace slag, fly ash and limestone have been studied. In these ternary binders, 30% of clinker has been equally replaced by two of those additions. As reference mortars, it has also been prepared specimens with ordinary Portland cement without additions, as well as specimens made with other three binary binders, with only one of the studied additions. The mortars were exposed to an optimum condition (20ºC and 100% relative humidity) until the testing age (28 days). The microstructure has been characterized using mercury intrusion porosimetry and electrical resistivity. Absorption after immersion and compressive strength have also been studied. According to the results obtained, mortars with ternary binders showed an adequate performance.

Keywords: ternary binders; eco-friendly cements; additions; ground granulated blast furnace slag; fly ash; limestone; sustainability; microstructure; mechanical properties; durability

1. Introduction

At present, in order to reach a more sustainable cement industry, several strategies have been put into practice. One of them is to increase the use of eco-friendly cements with lower content of clinker, replacing it by additions [1,2], such as ground granulated blast furnace slag, fly ash and limestone. In addition to the environmental benefits, some of these additions improve several properties of the cement-based materials [3,4]. As commercial cements, those made with binary binders, incorporating one addition as clinker replacement, are mostly produced nowadays. Nevertheless, the use of ternary binders, in which clinker is partially replaced by two additions, for manufacturing commercial cements is very low, at least in Spain. Therefore, to explore the performance of mortars and concretes prepared using cements made with ternary binders [5] could be a promising research field for giving more solutions to improve the sustainability of cement industry.

Then, the objective of this research is to study the short-term effects produced by ternary binders with the additions of ground granulated blast furnace slag, fly ash and limestone in the microstructure, durability and mechanical strength of mortars. Their behavior has been compared to that observed for mortars made with ordinary Portland cement without additions, as well as with other mortars made with binary binders, with only one of the studied additions.

2. Materials and Methods

2.1. Materials and sample preparation

Mortars prepared with different binary and ternary binders were studied. Reference mortars were made using ordinary Portland cement without additions, CEM I 42.5 R (Spanish and European standard UNE-EN 197-1 [6]), and they were designed as REF in the results and discussion section. Three binary binders were analyzed, in which 30% of the abovementioned cement CEM I 42.5 R was replaced by one addition. These binders were named as L, S and V, containing limestone, ground granulated blast furnace slag and fly ash, respectively. In addition to this, three ternary binders in which 30% of clinker has been equally replaced by two of the previously mentioned additions were also studied. The ternary binder designed as SL incorporated 15% ground granulated blast furnace slag and 15% limestone, and that named as SV included 15% ground granulated blast furnace slag and 15% fly ash. Finally, a last ternary binder with 15% fly ash and 15% limestone was also studied, being named as VL in the results description. In order to facilitate the comprehension of the meaning of the different designations established for the mortars, they are compiled in Table 1. The specimens of all the binders studied were prepared with water to binder ratio 0.5. Fine aggregate was used according to the standard UNE-EN 196-1 [7] and the aggregate to cement ratio was 3:1 for all the mortar series.

Table 1. Designation of the mortars studied and percentage of CEM I and additions

Designation	CEM I 42.5 R	Limestone	Blast furnace slag	Fly ash
REF	100%	-	-	-
L	70%	30%	-	-
S	70%	-	30%	-
V	70%	-	-	30%
SL	70%	15%	15%	-
SV	70%	-	15%	15%
VL	70%	15%	-	15%

Three different types of specimens were prepared. First of all two cylindrical specimens were made, a first type with dimensions 10 cm diameter and 22 cm height and a second one with dimensions 5 cm diameter and 6 cm height. Moreover, prismatic samples with dimensions 4 cm x 4 cm x 16 cm were made. Up to 24 hours from setting, all specimens were kept in 95% RH chamber and 20ºC. Once finished that time, they were de-moulded and stored under the same optimum condition until the testing age (28 hardening days).

2.2. Experimental tecniques

The pore structure of the mortars was studied using mercury intrusion porosimetry and non-destructive electrical resistivity.

The mercury intrusion porosimetry was performed with a porosimeter Poremaster-60 GT of Quantachrome Instruments (Boynton Beach, Florida, USA). Before the test, the samples were oven dried at 50°C for 48 hours. The parameters obtained with this technique which were analyzed, have been total porosity, pore size distribution and percentage of mercury retained at the end of the experiment. Two tests were made on each binder and the samples tested were pieces taken from cylindrical specimens with 5 cm diameter and 6 cm height.

The electrical resistivity provides data about pore connectivity in a cement-based material [8,9]. In this work, the non-destructive Wenner four-point test was used to obtain the resistivity of cylindrical specimens with dimensions 10 cm diameter and 22 cm height, according to the Spanish standard UNE 83988-2 [10]. This parameter was measured using a Proceq analyser at different ages up to 28 hardening days.

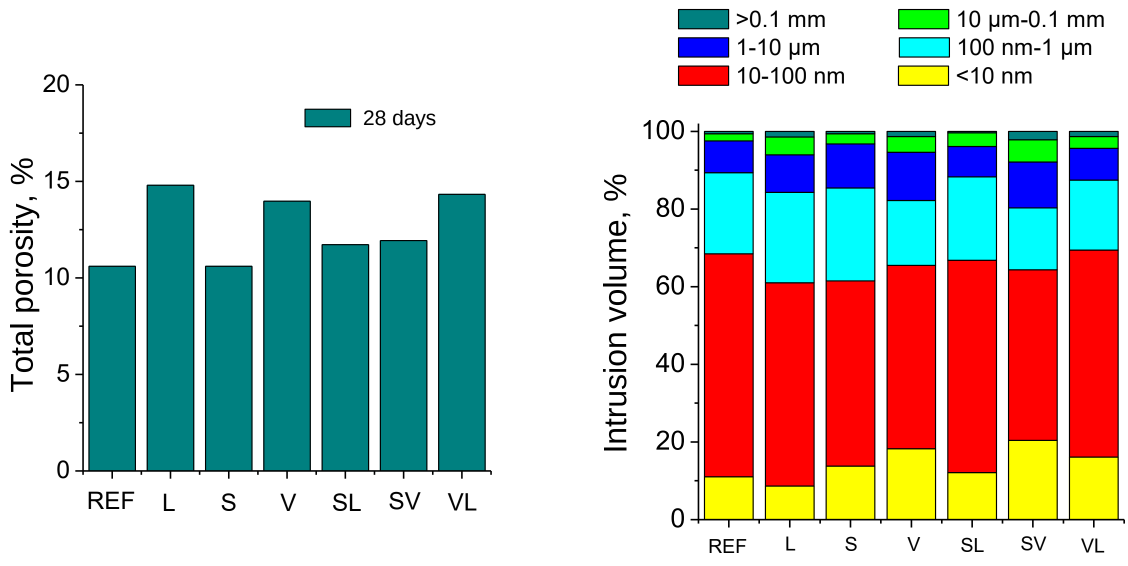
With respect to the properties of the mortars, the absorption after immersion and the mechanical strength were determined at 28 hardening days. The absorption after immersion was obtained following the procedure described in the ASTM Standard C642-06 [11]. Six pieces taken from cylinders with dimensions 5 cm diameter and 6 cm height were tested for each binder.

Lastly, the compressive strength was obtained in prismatic samples with dimensions 4 cm x 4 cm x 16 cm according the Spanish and European standard UNE-EN 1015-11 [12]. Three prismatic samples were tested at the studied age for each one of the analyzed binders.

3. Results and Discussion

3.1. Microstructure characterisation

In relation to mercury intrusion porosimetry technique, the results of total porosity are depicted in Figure 1.a. As can be observed, the lowest values of this parameter corresponded to series REF and S. The mortars made with ternary binders SL and SV showed slightly higher total porosities than those noted for REF and S mortars. On the other hand, the greatest total porosities were observed for binary mortars L and V and for the ternary binder VL. The lower total porosities of REF and S mortars would be indicative of the development of slag and clinker hydration [13,14], which started since setting once both slag and clinker are in contact with water. This effect was more evident in these mortars because no other components apart from clinker or slag were present in them. The higher total porosity noted for L specimens could be explained in the fact the limestone is not an active addition. Regarding V and VL binders, the larger porosities values could be due to the delay of the development of fly ash pozzolanic reactions [15], compared to clinker and slag hydrations. Therefore, it is expected that part of the beneficial effects of this addition would be more noticeable at later ages than 28 days.



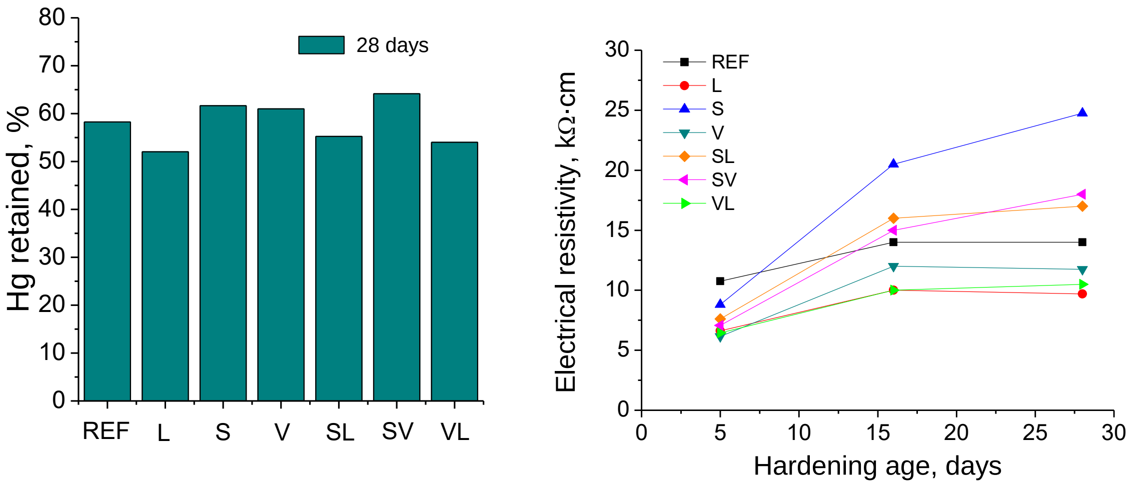
(**a**) (**b**)

Figure 1. (**a**) Total porosity results obtained for the studied binders; (**b**) Pore size distributions (in percentage) for the different types of mortars analyzed.

With respect to the pore size distributions, they are represented in Figure 1.b. The percentages of pores with diameters lower than 100 nm (pore ranges <10 nm and 10-100 nm) were relatively similar for all studied mortars. However, specimens with fly ash and ground granulated blast furnace slag showed higher relative volume of pores <10 nm, which would indicate a higher refinement of microstructure, probably due to formation of solid phases as products of slag hydration [13,14] and fly ash pozzolanic reactions [15]. This was especially noticeable for the SV binder, in which the abovementioned both active additions were incorporated, being more evident the synergetic effects of both additions in the microstructure development. Again, the less refined pore network corresponded to L mortars, which would be in keeping with total porosity results, showing the effect of this not active addition.

The results of percentage of mercury retained at the end of porosimetry test can be observed in Figure 2.a. This parameter provides qualitative information about the tortuosity of the pore network of the materials. The higher values of this parameter were noted for S, V and SV mortars, suggesting a more winding and refined microstructure. They were followed by REF, SL and VL binders with a slight lower percentage of mercury retained. In the ternary binders SL and VL, the presence of limestone could explain the scarce lower tortuosity and pore refinement observed. Finally, the lowest percentages of mercury retained have been noted for L mortars. The results of this parameter were overall in agreement with those obtained for total porosity and pore size distributions.

The electrical resistivity results are depicted in Figure 2.b. This parameter provides data about the connectivity of pores as well as the evolution of the microstructure [16]. The increasing tendency of this parameter for all the mortars studied would reveal the progressive development of their microstructure, due to a reduction of pores with higher diameters, as a consequence of the solid phases formation. At 28 hardening days, the highest values of the electrical resistivity were noted for binders with slag (S, SV and SL series). This would indicate the effects of slag hydration, which were more noticeable for this parameter, at least in the short term.



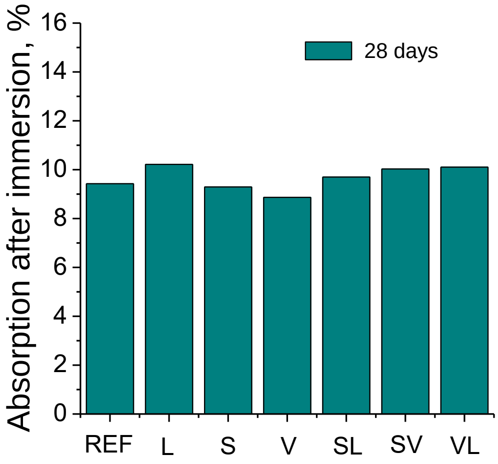
(**a**) (**b**)

Figure 2. (**a**) Results of Hg retained at the end of mercury intrusion porosimetry test for each one of the binders studied. (**b**) Evolution of the electrical resistivity for the analyzed mortars.

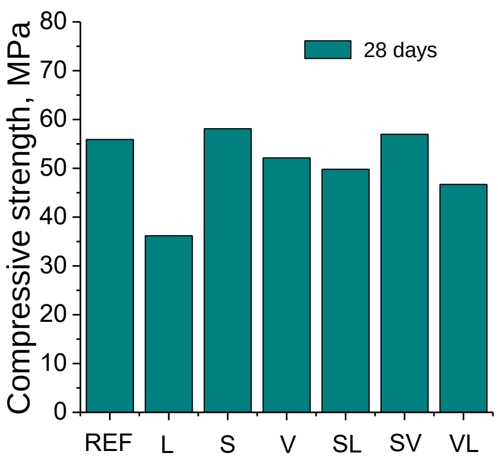
3.2. Durability and mechanical properties

As durability parameter, the absorption after immersion has been studied. The results of this parameter are shown in Figure 3.a. This parameter was relatively similar at 28 hardening days for all the mortars studied, being slightly higher for ternary binders and L mortars, compared to REF, S and V mortars. However, it can be indicated that the behavior of the studied binders was overall adequate regarding the water absorption.

The compressive strengths results are depicted in Figure 3.b. The highest values of this parameter were observed for REF, S and SV specimens. This would show again the good performance at 28 hardening days of the ternary binder which combined slag and fly ash, probably due to the synergetic effects of slag hydration [13,14] and fly ash pozzolanic reactions [15] in the formation of new solid phases, improving the strength of the material. The lowest compressive strength was noted for L specimens, which would coincide with the results of microstructure characterization. In addition to this, the addition of limestone produced in the ternary binders (series SL and VL) a reduction of the compressive strength compared to binary binders only with slag or fly ash (S and V series).



(**a**)



(**b**)

Figure 3. (**a**) Results of absorption after immersion for the studied mortars; (**b**) Compressive strength results obtained for analyzed binders.

4. Conclusions

The main conclusions that can be drawn from the results previously discussed can be summarized as follows:

- The lowest total porosity values were noted for reference mortars and for those made with binary binder which only contained slag. This could be due to the development of slag and clinker hydration and it would be most noticeable in these mortars because they were the series with higher content of clinker and slag.
- The highest total porosity, the lowest pore refinement, the lowest electrical resistivity and the smallest compressive strength have been observed for binary mortars with the only addition of limestone. This could be explained in relation to the fact the limestone is not an active addition, so its beneficial effects in the microstructure and properties development is limited compared to slag and fly ash.
- Mortars with fly ash and ground granulated blast furnace slag showed higher refinement of microstructure, which was especially noticeable for the ternary binder with both slag and fly ash additions This would highlight the synergetic effects of combining both additions in the microstructure development.
- The absorption after immersion parameter was relatively similar at 28 hardening days for all the mortars studied, so regarding the water absorption, the performance of the studied binders was overall adequate.
- The compressive strengths results also revealed the good performance at 28 hardening days of the ternary binder which combined slag and fly ash, which would probably related to the synergetic effects of slag hydration and fly ash pozzolanic reactions in the formation of new solid phases, improving the strength of the material.
- The addition of limestone in the ternary binders entailed a reduction of the compressive strength compared to binary binders only with slag or fly ash.

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

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