TÉCNICO LISBOA

Performance of cementitious materials with reactive magnesium oxide, slag and recycled aggregates

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Master Thesis in Civil Engineering

Extended Abstract

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1 Introduction

Nowadays, the construction sector has a high environmental impact. The cement industry is responsible for about 5% to 7% of the global emissions of carbon dioxide (CO_2), according to Benhelal *et al*. (2013). In order to minimize the ecological problem of cement production, several sustainable alternatives have been proposed and studied over the years.

In addition to CO_2 emissions and raw material needs, this sector generates a huge amount of Construction and Demolition Wastes (CDW), comprising materials such as concrete, tiles, ceramics, plastic, wood, glass, bituminous mixtures, metals and even soil.

CDW represent approximately 36% of the total waste produced on the planet (Bui *et al.,* 2018). Contextualizing, in the United States of America alone, the amount of CDW produced increased from 50 million tonnes (1980) to 548 million tonnes (2015) (Butler *et al.,* 2011). In China the annual production of CDW exceeds 1.5 billion tonnes (Poon *et al.,* 2007). In addition, in Europe, the production of this type of waste reaches about 850 million tonnes/year, representing 31% of the total waste in the EU (Mahmoud *et al.,* 2020).

Since cement is the main constituent of mortars, and therefore the most polluting component, it motivates the study of new alternatives to replace the traditional cements currently used.

Consequently, in addition to alternatives to Portland cement, the incorporation of fine recycled aggregates (RA) as a total replacement of fine natural aggregates (NA) is also studied. RA from CDW, and mostly composed of concrete, masonry and bituminous materials, were used.

The motivation of this dissertation is the replacement of Portland cement (partially or totally) in mortars with other more sustainable alternatives. Two materials were used: reactive magnesium oxide (MgO) and blast furnace slag. These materials have a smaller ecological footprint, since, in the case of slag, it is a by-product of the steel industry that can be reused.

However, it is necessary to assess the effects that the use of MgO and slag, together with fine RA, cause on the performance of mortars over time. So, some of the properties that characterize mortars, both in terms of mechanical strength and durability, will be studied throughout this Dissertation.

2 Experimental campaign

The main objective of this dissertation is to evaluate the feasibility of incorporating MgO and blast furnace slag as partial substitutes for Portland cement and fine RA for the production of mortars. For this purpose, different mortars will be produced, with different amounts of MgO and slag incorporated in them. The amounts of these materials to be used will be 0%, 10% and 20%, respectively, while the fine RA will be used in amounts of 0% and 100%. It should be noted that the study will mainly focus on the use of the two materials mentioned above and fine RA simultaneously, but all the materials will also be analysed individually, to understand better their joint action.

With regard to MgO, two types of MgO will be used. The first, Australian, is very reactive (MgO-A) and the second, of Spanish origin, has a low reactivity (MgO-E). Both MgOs will be used in equal amounts.

Characteristics regarding mechanical strength as well as durability will be analysed. The mixes

will also be analysed during the fresh state, through the study of workability and density.
Curing in carbonation chamber will also be analysed in order to understand the influence of this type of curing on mechanical strength and durability, compared to curing in a wet chamber.

2.1 Materials

The aggregates used in this experimental campaign were fine natural aggregates and fine recycled aggregates. The fine recycled aggregates, in its turn, used in the mortars come from construction and demolition wastes (CDW).

The cement used in the mixes was the CEM I 42.5R. Two different types of MgO were also used: Australian MgO, designated by MgO-A, and Spanish MgO, designated by MgO-E. Both oxides are used in equal percentages. Along with MgO, slag was also used, in order to contribute to the use of a higher percentage of cement replacement.

2.2 Procedures

The experimental campaign was organized into several phases. Firstly, the aggregates and binders were characterized. After that, the various mixes that were cast were analysed. Fresh concrete tests were performed and, for different ages of the specimens, tests were performed on concrete in the hardened state. All tests were performed considering the specifications of the European standards, in order to allow comparability with other studies.

3 Results and discussion

3.1 Properties of aggregates

The test of water absorption of natural aggregates (pycnometer test) determines the value referring to an immersion for 24 hours. The results obtained, and presented in Table 1, for fine sand, coarse sand and fine AR were 0.3%, 0.7% and 10.2%, respectively.

Table 1 also presents the density of the aggregates used.

Table 1 - Properties of aggregates

Density (kg/m³)	**Material**		
	Fine Sand	*Coarse Sand*	*Fine RA*
ρ_a	2603.9	2626.3	2650.5
ρ_{rd}	2583.2	2581.4	2064.8
ρ_{ssd}	2591.2	2598.5	2159.0
Water absorption (%)	0.3	0.7	10.2

3.2 Properties of binders

Using X-ray diffraction (XRF), it was possible to determine the chemical composition of each material used to form the binder. The cement used (CEM I 42.5 R) has a high amount of calcium oxide (64.8%) and silica (18.1%). In slag, as expected, the oxides that are present in greater quantity in its constitution are the calcium oxide (28.2%) and ferric oxide (28.5%). MgO-A has higher specific surface area, higher purity and, consequently, higher reactivity, than MgO-E.

Reactivity is an important characteristic for the performance of mortars with MgO incorporation, because the lower is the reactivity of an MgO sample, the slower will be its hydration, and the slower will be the strength gain. The smaller specific surface area causes more agglomeration of particles in a sample, which leads to less hydration (Mo, 2010; Jin and Al-Tabbaa, 2014).

3.3 Fresh-state properties

Since the studied mortars can be considered micro-concrete, and it is important to ensure good workability, therefore, 200 ± 50 mm was adopted as an adequate consistency in this Dissertation. The water/binding ratio considered for mortars with fine NA was 0.49 and it was adjusted whenever necessary, in order to obtain the workability mentioned above.

When integrating fine RA, it was proved necessary to increase the amount of water to maintain the workability and, consequently, the water/binder ratio of the mortar. A ratio of 0.69 was considered for mixes with fine RA. Silva *et al.(*2016) found the same necessity in their study, and attributed this trend to the greater water absorption capacity, greater angularity and less fineness of fine RA, when compared to fine NA.

Regarding the density in the fresh state, both mortars containing fine RA and those containing fine NA maintain the same trends.

In both types of mortars, the density decreases with the increase in the ratio of replacement of cement with alternative binders, but the decrease is much less pronounced in mortars with fine RA.

3.4 Properties in the hardened state

3.4.1 Mechanical strength

The tests were carried out as described in the European standard EN 1015-11 (1999), and were repeated at 7, 28 and 91 days of age for each mortar.

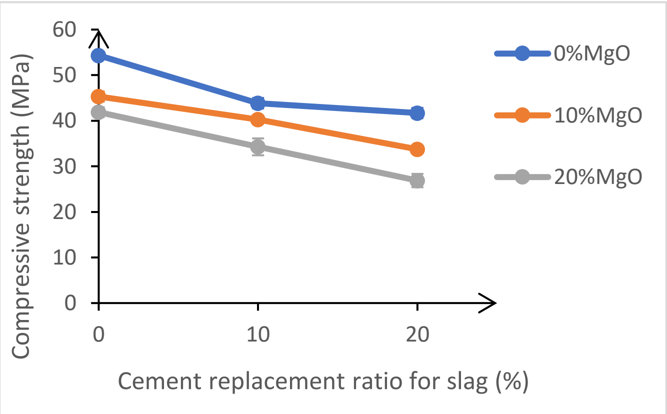

Figure 1 - Compressive strength at 28 days

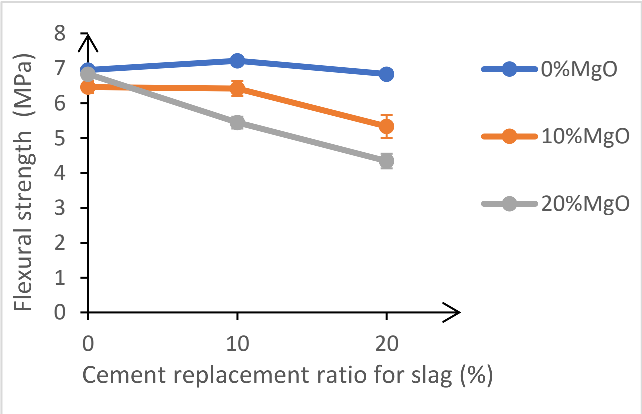

Figure 2 - Flexural strength at 28 days

When analysing Figures 1 and 2, it can be concluded that both compressive and flexural strengths, at 28 days of age, decrease with increasing MgO and slag contents.

However, it should be noted that, when cement is replaced with 20% MgO, the strength is very similar to the reference mortar for both tests.

The values obtained at 28 days of age are consistent with the results obtained by Gonçalves *et al.* (2020). At this age, the authors obtained a decrease in resistance of approximately 21.2%, for a partial replacement of 20% of MgO, while in this experimental campaign a decrease of 23% for an incorporation of 20% of MgO was obtained.

Mo *et al.* (2015) concluded that, as the curing time increases, the difference in strength between the reference mortar and the mortar with MgO tends to decrease. In fact, in the present investigation, it is also observed that, over time, the variation between the compressive strength in MgO-containing mixes and the reference mortar tends to decrease. At 7 days, the mixes with MgO present between 17% (incorporation of 10% of MgO) and 23% (incorporation of 20% of MgO) of compressive strength loss, in relation to the reference value. However, at 91 days, this strength reduction varies between 13% (10% of MgO) and 25% (20% of MgO). In the case of flexural strength, the variation compared to the reference mortar even increases with increasing curing time.

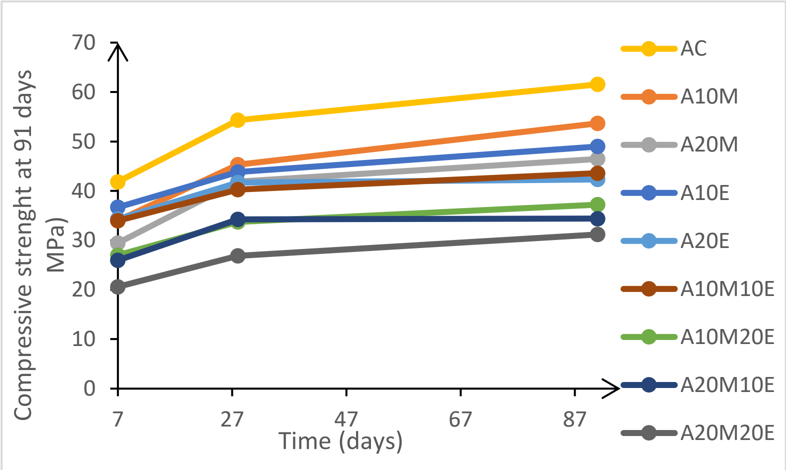

Figure 3 - Compressive strength at 91 days

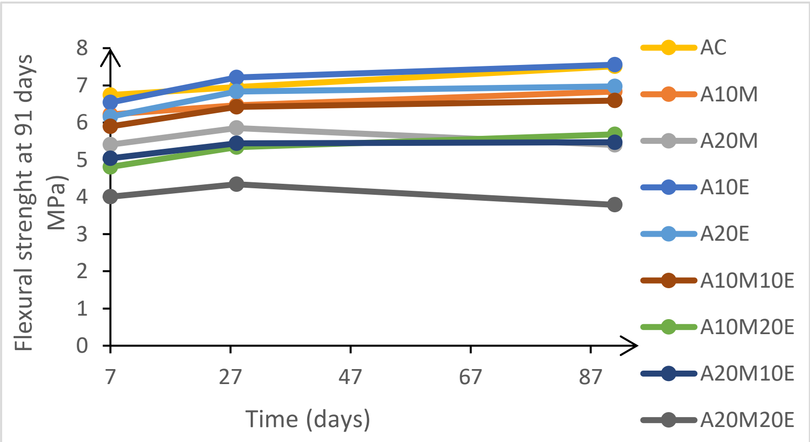

Figure 4 - Flexural strength at 91 days

Analysing Figures 3 and 4, it is noticeable, in general, that over 91 days all mortars similarly improve their strengths, both in compression and in flexural, except for mortar A20M20E, in which there is a decrease of flexural strength from 28 to 91 days.

It is noteworthy that the A10E mortar, which incorporates 10% of slag, presents a 1% increase, in relation to the reference mortar, of its flexural strength at the end of 91 days of curing. In turn, the 20E mortar showed a decrease of only 7% of the compressive strength at 91 days, compared with the reference mortar. These results, despite being very close, do not confirm the increases in strength obtained by Yun *et al.* (2020). These authors report that the optimal percentage of replacement of cement with slag is 40% and that this replacement increases the strength of cementitious materials by about 3% and 12% at 28 and 90 days of curing, respectively.

It is possible to conclude that, in general, with the replacement of fine NA with fine RA, with a simultaneous increase in the amount of MgO and slag, the compressive strength tends to decrease. It can also be concluded how each binder, individually and together, affects mortars with fine NA and those containing fine RA. Firstly, when 10% MgO is incorporated, this binder has a less significant effect on mortars with fine NA than with fine RA, at 7 and 28 days of age, with a tendency to stabilize at 91 days. With 20% MgO, a slight increase in the loss of strength of mortars with fine RA is noticeable: losses of 30%, 35% and 30% at 7, 28 and 91 days, respectively, when compared with those of fine NA, displaying losses of 30%, 23% and 25% at 7, 28 and 91 days.

When considering slag individually, it is notable that this material affects more the fine RA mortars, as well as when considering the two binders simultaneously. It is noted that mortars containing fine RA suffer greater loss of compressive strength at the three ages than those containing fine RA.

It is also concluded that, in both the compression and flexural strength results, there is an increase in strength with increasing curing time in a carbonation chamber. It can then be concluded that this type of curing promotes the strength development of mortars with RA.

3.4.2 Modulus of elasticity

There is an approximately linear decrease of this property with the increase in MgO and slag. The results are consistent with the study of Sequeira *et al.* (2021), where the authors found out that the loss of modulus of elasticity achieves the greatest reduction in concrete mixes with 20% of MgO in their constitution. These values reach reductions of 6.7% (MgO-S) and 14.6% (MgO-A), respectively. The reductions in question are insignificant. The authors state that, between 5% and 20% of MgO, this reduction occurs practically linearly.

After a comparative analysis between the effects caused by each of the materials individually, and simultaneously, it is necessary to analyse how they affect mortars with and without RA.

Incorporating MgO does not seem to have a great impact, since the modulus of elasticity varies in a similar way in mortars with and without fine RA.

In the case of slag, when integrated individually and simultaneously with MgO, it affects more the mortars with fine RA. The modulus of elasticity of these mortars displays more accentuated decreases than those containing fine NA.

Finally, it is analysed how carbonation influences this property in mortars that contain 100% fine RA. It should be noted that, in mortars that contain only MgO, carbonation has a positive influence. Both in carbonation at 14 days and at 28 days, the A10M-R and A20M-R mortars show improvements when compared to the reference mortar.

3.4.3 Ultrasonic pulse velocity

It appears that the integration of these two binders, individually and together, has a negligible influence on the ultrasonic pulse velocity at 28 days.

With regard to mortars that incorporate fine RA, when incorporating MgO, it does not seem to have a great impact, since the ultrasound velocity varies in a similar way in both mortars with and without fine RA.

In the case of slag, when integrated individually and simultaneously with MgO, it affects more the mortars with fine RA. However, there is a very slight decrease in ultrasound velocity when compared to mortars without fine RA.

Finally, it can easily be concluded that, in general, carbonation acts positively on this property.

At 14 days of carbonation, it is found that the variations of the various mixes when compared to the variations of the mixes that did not undergo carbonation are slightly lower. At 28 days of carbonation, these differences are more pronounced.

3.4.4 Water absorption by capillarity

When considering a partial replacement of 20% of MgO and 20% of slag, a relative minimum is obtained, i.e. the lowest rate of water absorption by capillarity. It is thus concluded that the two binders, simultaneously, present a better performance than individually.

When integrating MgO individually, mortars with and without fine RA present similar increases in water absorption by capillarity: around 11% and 40% for incorporations of 10% and 20% of MgO in mortars without fine RA, and 13% and 35% for incorporations of 10% and 20% MgO in fine RA mortars, respectively.

When slag is integrated, there is a marked decrease in the ability to absorb water by capillarity in mortars containing fine RA, when compared to fine NA mortars.

The former increase the absorption capacity by about 21% and 23% for incorporations of 10% and 20% of slag, while the latter increase by about 74% and 59% for incorporations of 10% and 20%. Individually, slag along with fine RA favour this property.

By integrating MgO and slag at the same time, mortars with fine RA are favoured, as they generally present a lower increase in absorption capacity than mortars with fine NA.

It can be concluded that all mixes that contain fine RA, MgO and slag simultaneously, with the exception of A10M20E-R, present better results than expected, since the variation obtained is lower than the variation estimated (value obtained by the sum of the individual effects of each material).

3.4.5 Water absorption by immersion

It can be inferred that the water absorption by immersion increases linearly with the increase of MgO and slag, except for mortars that contain 10% of MgO.

When integrating MgO individually, mortars with and without RA present very different increases in water absorption by immersion, about 61.9% and 80.5% for incorporations of 10% and 20% of MgO in mortars without fine RA and 5.1% and 6.1% for incorporations of 10% and 20% of MgO in RA mortars.

When slag is integrated individually, there is also a marked decrease in the ability to absorb water by immersion in mortars containing RA, when compared to mortars with NA. The former increase the absorption capacity by about 13.7% and 14.4% for incorporations of 10% and 20% of slag, while the latter increase by about 37% and 52.4% for incorporations of 10% and 20%. Individually, MgO and slag, together with fine RA, favour this property. By integrating MgO and slag at the same time, mortars with fine RA continue to be favoured, as they generally present a much smaller increase in absorption capacity than mortars with fine NA. For mortars with RA increases of 21.4%, 13.0%, 17.5% and 39.2% were obtained, compared to 44.7%, 90.0%, 110.0% and 120.0% for mortars with fine RA.

When analysing the effect of carbonation on this property, it appears that carbonation does not have as significant contribution as in the other properties. Some mortars exposed to carbonation even increase their water absorption capacity when compared to non-carbonated mortars.

3.4.6 Carbonation depth

By incorporating MgO individually, it can be seen that there is a more pronounced increase in carbonation depth in mortars with fine NA than in those containing fine RA. When considering slag individually, the same trend is no longer observed, as it affects more mortars that contain RA. When considering the two materials at the same time, it can be concluded from the results that it affects both mortars with and without RA in a similar way.

3.4.7 Shrinkage

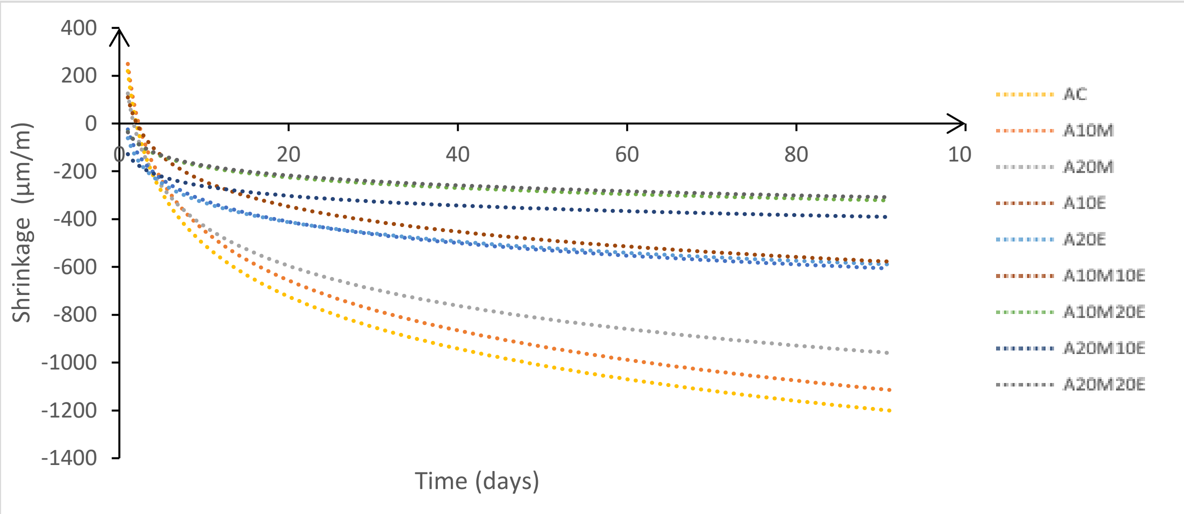

Figure 5 - Shrinkage at 91 days

By analysing Figure 5, as the percentage of MgO increases, the shrinkage at 91 days decreases and slag also contributes to a greater decrease in shrinkage depending on the respective increase. When both materials are incorporated at the same time, the same trend is maintained, but the "minimum" shrinkage is obtained for two mortars: A10M20E and A20A20E. This allows concluding that, when 20% of slag is incorporated, the incorporation of 10% or 20% of MgO assumes an unimportant role in terms of reducing this property.

When replacing fine NA with fine RA, shrinkage increases substantially, with the exception of the A20M-R mortar. This trend was also observed in the studies of Neno *et al.* (2014) and Silva *et al*. (2015). According to Neno *et al.* (2014), the increase in shrinkage related to the use of fine RA is due to the fact that RA are more porous than NA, which makes the mortar resulting from the incorporation of the former have less rigidity than that with incorporation of the latter. If the stiffness of the mortar decreases, then there will be a greater tendency to accompany and accentuate the shrinkage of the cementitious matrix.

In the case of mortars containing fine RA, the integration of MgO individually contributes to a greater decrease in shrinkage: around 41% and 64% for 10% and 20% of MgO than for mortars made up of fine NA, around 9% and 24% for the same replacements.

In the case of slag, the same trend is no longer observed. It shows a decrease of only 16% for both 10% and 20% replacements for mortars with fine RA, while for mortars with fine NA there is a decrease of 55% and 58% for the same percentages of replacement of binder.

When the two materials are considered together, the results do not correspond to the expected ones, with shrinkage increases of 4% and 7% for mortars A10M20E-R and A20M20E-R, respectively. With this, it can be concluded that these two materials together with the RA do not benefit this property.

4 Conclusion

The research developed was intended, as indicated in Chapter 1, to deepen the knowledge on the use of MgO and slag as partial substitutes for Portland cement, and recycled aggregates in the production of mortars. The objective was to understand the influence of MgO, slag and recycled aggregates on the mechanical performance and durability of mortars.

Mortars that contain only MgO present, in general, with the exception of shrinkage, lower results than those obtained by the reference mortar. The same trend can be seen when considering only the use of slag.

Thus, it should be noted that, when incorporating these two materials individually, the only property benefited is shrinkage, which, for example, decreases significantly by half when slag is incorporated into the mix (by 10% or 20%).

When considering the two materials at the same time, there is a greater difference in values, compared to the reference mortar.

One of the main reasons to study the use of MgO as a binder in mortars or concretes is its ability to reduce the shrinkage of cementitious materials. However, it can sometimes cause harmful initial expansion when hydrated. In this study, a mixture of 2 MgOs, of different reactivity, was considered in order to understand their behaviour together. Taking into account the shrinkage results of all mortars that incorporate MgO, it appears that, when MgO was incorporated (whatever the percentage used), the respective mortars showed lower shrinkage results than the reference mortar.

However, the results obtained by mortars that incorporate slag were even more positive. The slag, when considered individually, contributed to a much more significant decrease in shrinkage than that observed in mortars with MgO. Perhaps these results are justified by the mixes of MgOs, since the less reactive MgO may have reduced the expansive capacity of the more reactive MgO. When incorporating the fine AR, a set of trends similar to the one verified in the mortars with NA is verified, so, when incorporating MgO and fine RA in the mixes, the losses are quite similar to the mortars where the use of fine RA is not considered. Thus, the junction of the two materials contributed to a lower absorption of water by immersion and to a more accentuated decrease in shrinkage.

When considering the simultaneous use of fine slag and RA, it appears that the trends are similar to those obtained for mortars with fine NA. However, it should be noted that the losses are much more accentuated in mortars that contain fine AR, with the exception of tests on water absorption by capillarity and immersion, in which considerably lower water absorptions are obtained. The combination of these two materials also contributed to an increase in shrinkage, compared to that observed in mortars with thin NA.

In mortars that incorporate the two binders and fine RA, there is an overlapping of effects, which results in a much more accentuated difference, compared with the reference mortar and with the same mortars containing fine NA in their constitution. Therefore, the use of the three materials simultaneously presented the worst performances. This trend was not observed in the capillary and immersion water absorption tests.

In the present dissertation, the influence of carbonation curing, compared to wet curing, on the development of mechanical strength and properties in terms of durability of mortars was also evaluated.

In general, the curing with exposure to carbonation of mortars with MgO and/or slag contributed to a less pronounced loss of mechanical strength than that observed in the same mortars exposed to wet curing.

When considering mortars that contain fine AR in their constitution, it can be seen that curing with exposure to carbonation of these mortars does not bring benefits.

5 References

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