TÉCNICO LISBOA

ALKALINE TREATMENT APPLIED TO RICE HUSK TO PRODUDE CEMENT-BASED COMPOSITES

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Extended Abstract

The concept of sustainability is increasingly associated with the civil engineering sector. However, the construction sector is one of the most damaging to the environment. It contributes daily to its degradation through high energy consumption and the excessive use of materials extracted from nature. In this context, the present study's main theme is related to the introduction of rice husk, with and without treatment, in cementitious composites, working as a light aggregate, to take advantage of the good acoustic and thermal characteristics that this agricultural by-product offers. Rice is one of the most cultivated and consumed cereals globally, which consequently results in the existence, on a large scale, of its protective layer. However, because the rice husk has no use at all, due to its inherent characteristics, its purchase price is quite low, encouraging the purchase of this material. To improve this type of material's less positive characteristics, an alkaline pre-treatment of the rice husk using sodium hydroxide was developed throughout this study. This treatment's main objective is to eliminate part of the existing organic matter that is harmful to the cement composites to be produced, improving their characteristics. Special thanks to the 'RiceHusk+' project and Farcimar company for their support.

Keywords: Rice husk; Alkaline treatment; Sodium hydroxide; Cementitious composites;

1 Introduction

One of the main concerns nowadays is the reduction of environmental impacts from the most diverse sectors of current society. Unfortunately, the construction industry, and all those associated with it, are no exception, contributing daily to the degradation of the environment and the increased risks caused by global climate changes. In this context, there is a need to implement measures that will benefit a sustainable strategy and minimize the less positive impacts that this sector has on the environment.

The introduction of solutions, such as rice husk (RH), in different building materials, has emerged as an important sustainability strategy since their use in place of the commonly used fibers (e.g., glass, asbestos, polymeric fibers...) allows the reduction of economic costs and environmental impacts related to their production [1]. This study will be based on a detailed analysis of the RH, and all the advantages that this type of by-product can offer can be presented when applied in cementitious composites. Finally, with this study, it is also intended to demonstrate that RH and all other products of this nature will present themselves shortly as an excellent opportunity to develop solutions with innovative and distinctive features in the global market.

2 Theoretical concepts

2.1 Natural Fibers

Recently, there has been an increasing interest in the incorporation of natural fibers into cementitious composites. This is assumed to be related to composites' nature, the potential improvements that fiber properties can offer, or even society's growing concern to preserve nature and the environment. Unlike human-made fibers, which have perfectly defined geometry, surface characteristics, mechanical, physical, and chemical properties, natural fibers have identical main characteristics but without uniformity between the various parameters presented [2].

Natural fibers are classified according to their origin and can be subdivided into three groups: vegetable, animal, or mineral. However, only vegetable fibers will be considered in the present study since this is the group in which the rice husk (RH) is included.

2.2 Rice husk characterization

Formed during rice grains' growth, this protective layer has as its main characteristics of low density and high porosity. Internally and according to previous studies, it can be deduced that RH is composed of multiple constituents, which in its structure include about 45-50% cellulose, 25-30% lignin, and 15-20%silica [3]. A schematic image of the composition of a grain of rice is shown in figure 2.1.

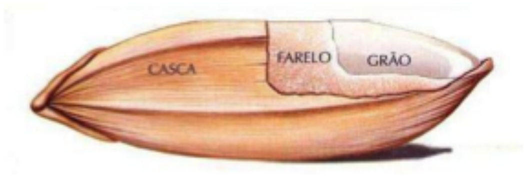


Figure 2.1 - Illustration of a grain of rice and its constituents. Adapted [3].

RH has a significant silica concentration, limiting the interest of farmers/producers in this raw material. One of its possible applications would be to use the husk resulting from rice production as food for the most diverse types of animals. However, and due to this explanation, this is not possible since its chemical composition makes its nutritional properties weak and harmful for animals. In this way, and with no viable destination for its application, producers are forced to deposit the RH in landfills to be subsequently burned, generating negative and damaging environmental effects [1]. After this brief explanation, it is justified that the RH has a low commercial value, which encourages its use as a total or partial substitute for conventionally used aggregates.

2.3 Principal advantages and disadvantages of rice husk

The main advantages of RH are related to its morphological structure and its acquisition cost. Since RH's incorporation was not intended to serve as a mechanical reinforcement, its low density, rigidity, and porosity give it good acoustic and thermal insulation properties, as intended. On the other hand, using RH has a positive influence on the economy and culture. The preference for this material will enhance the value of natural resources and contribute to the agro-industry rice production [4].

The main disadvantages associated with the RH are related to its chemical structure. The fact that the RH is mainly composed of cellulose gives it hydrophilic characteristics [5], which can be a problem in the formulation and manufacture of cement-based composites. Also related to their composition, another negative aspect that vegetable fibers have is the lack of adhesiveness between fibers and cement due to oils and other organic matter on their surface.

2.4 Alkaline treatment

According to [6], the treatment consists of immersing the fibers in an aqueous solution with a strong base for a certain period of time, allowing the removal of materials containing lignin, pectin, waxy substances, and natural oils that cover the external surface of the fiber cell wall. The reagent used was sodium hydroxide (NaOH), one of the chemicals commonly used in this type of process, since it makes it possible to clean and bleach the surface of the fibers.

The reaction occurs between the OH- present groups in the cellulose fibers and NaOH through the interruption of the hydrogen bonds existing in the cellulose network structure [7], as shown in figure 2.2.

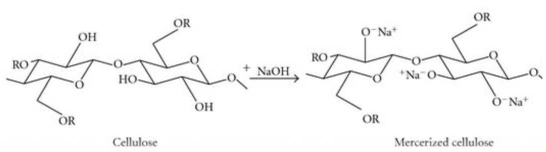


Figure 2.2 - Cellulose structure before and after alkalinization treatment. Adapted [8].

This transformation results in the necessity of hydroxyl (OH-) groups to form new bonds with the water molecules, causing swelling of the cell wall, allowing large chemical molecules to penetrate the crystalline regions. Consequently, the fibers' surface roughness increases, amplifying the number of anchorage or reaction points, providing improvements in the mechanical interaction with the matrix, ultimately contributing to a better interfacial bond [9].

3 Experimental methodology

3.1 Definition of the experimental program

The experimental campaign has been defined based on previous studies. Some of these studies and the methodologies used are presented in table 3.1.

Table 3.1 – Alkaline treatment applied to several vegetable fibers.

Material	NaOH	Duration	Ref
Sisal	5%; 10%	48h	[9]
Flax	4%; 6%; 8%	1h	[10]
Hemp	3%; 6%; 9%	48h	[11]
RH	2%; 4%; 6%; 8%	4-5h	[12]
Bamboo	10%	1h	[13]

According to the previous researches, it was defined that the present study would be divided into three experimental campaigns to approach different modes, intensities, and duration of treatment. In this context, the three idealized campaigns and their respective treatment processes are presented in table 3.2.

Table 3.2 - Experimental campaigns adopted in this study.

Campaign	NaOH	Duration
1st	0%	2h
2nd	6%	1h, 2h, 4h
3rd	3%, 9%	2h

It was in the first experimental campaign that the reference composites were produced. These composites served as a starting point for the present study since the rice husk (RH) used in their production was not subjected to any treatment. By comparing the results obtained in this campaign with the others, the influence of the alkaline treatment was evaluated.

In the second experimental campaign, an initial concentration of 6% of NaOH was considered since the results obtained by the authors [10], [12] suggested that this was the concentration that would lead to the most balanced results. The immersion periods ranged from 1h, 2h, and 4h to understand the influence that the treatment period has on the RH.

The third and final experimental campaign was defined, but this time, NaOH concentration varied, and the duration applied was defined according to the results obtained in the second experimental campaign. Therefore, the concentrations considered were 3% and 9%, considered the minimum and maximum limits for treating fibers with these characteristics [11], [12].

3.2 Composites produced during the three campaigns

During the three experimental campaigns, were produced pastes and mortars. All the pastes developed during the three experimental campaigns were produced with leaches from the various treatments applied to the RH. During the beginning of the cement hardening process, the RH releases leachate into the mixture, allowing an eventual interaction of some harmful products with the cement. It should be noted that this incompatibility will tend to be higher for pastes produced with leachate from untreated RH or treatments of lower intensity. Therefore, the main objective for the production of pastes was to analyze the impact leachate from the various types of treatment and immersion periods may have on the composites to be produced.

The main purpose of producing mortars was to evaluate how RH interacts with the cement matrix and its bonding, depending on the different alkaline treatment processes developed during the various experimental campaigns. Through the results obtained in the tests performed on these composites, it will be possible to analyze if the alkaline treatment allowed the less positive characteristics of the RH to be counteracted and if with its application there were improvements in the acoustic and thermal insulation properties that this agro-industrial by-product offers.

3.3 Tests applied to the composites produced

Throughout this study, several tests have been applied to the composites produced. In this context, the principal tests performed on the pastes and mortars produced are presented in tables 3.3 and 3.4, respectively.

Table 3.3 - Tests applied to the pastes, performed for each age, according to the respective standards.

Test	Age	Standard
Fresh density and workability	0	NP EN 1015-6 NP EN 1015-3
Consistence and setting time	0	NP EN 196-3
Determination of total and open porosity	28 days	NP EN 1936-2008
SEM	28 days	-
Mechanical strength measurement	7, 28 days	NP EN 1015-11

Table 3.4 - Tests applied to the mortars, performed for each age, according to the respective standards.

Test	Age	Standard
Fresh density and workability	7, 28, 90 days	NP EN 1015-6
Determination of total and open porosity	28, 90 days	NP EN 1936-2008
Ultrasounds	28, 90 days	-
Dynamic Young's Modulus…	28, 90 days	ASTM E1876-01
Wet/drying cycles	28, 90 days	-
SEM	28 days	-
Mechanical strength measurement	7, 28, 90 days	NP EN 1015-11

In addition to the tests presented before, chemical analyses of the leachate used in the production of the pastes and some characterization tests on RH were performed. Therefore, the exposition of the results achieved during the three experimental campaigns will start with presenting the results obtained in some of the characterization tests applied to the RH.

4 Results and discussion

4.1 Granulometry analysis

The granulometric test was performed according to the EN 933-1:2014 standard. The test was realized to determine the majority size ranges and the distribution of the material under study. In this context, the layout of the rice husk (RH) granulometric curve obtained after the test is shown in figure 4.1.

Figure 4.1 shows that approximately 90% of the particles have dimensions between 1 and 4 mm. It should be mentioned that this test was applied to RH after being dried, and there was no selection in the particles to be tested.

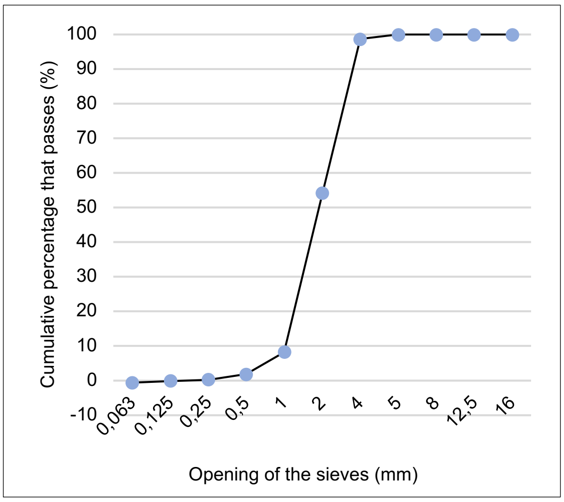


Figure 4.1 - Granulometric curve of rice husk.

4.2 Determination of loose bulk density and voids

The intention of this test was to evaluate the effect that alkaline treatment has on RH morphology. The RH was treated with 0%, 3%, 6% and 9% for a period of 2 hours. The results are shown in table 4.1.

Table 4.1 Results obtained in the loose bulk density and voids test.

NaOH concentration	Bulk density and voids (kg/m^3)
0%	190
3%	200
6%	220
9%	320

Through the analysis of table 4.1, as the concentration of NaOH increases, the parameter under analysis tends to grow, which means that it was possible to deposit a larger quantity of material for the same volume. As will be seen in the next subchapter, the increase in

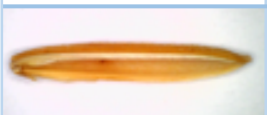
NaOH concentration causes a morphological change in the RH by making the particles more oval and less long, resulting in a decrease in the number of voids. From these results, it is believed that mixtures produced with RH treated with higher NaOH concentrations will have better workability levels.

4.3 Rice husk images captured with a binocular magnifying glass

To complement the conclusions presented above, rice grains' images after being treated with concentrations of 0%, 3%, 6%, and 9% NaOH are shown in table 4.2.

As previously explained, the increased concentration of NaOH causes some changes in the morphology of the RH, as can be seen from the images presented. These changes result from the process explained in [9] since the swelling of the RH particles' walls causes their sides to begin to open and their tops to shrink to follow this transformation process.

Table 4.2 - Morphological modifications verified on the rice husk.

Images	NaOH	Dimensions
	0%	L_1= 8,00 L_2= 0,78
	3%	L_1= 7,93 L_2= 1,04
	6%	L_1= 7,78 L_2= 1,40
	9%	L_1= 7,57 L_2= 1,51
Legend: L_1 – Lenght; L_2 - Width		

4.4 Chemical analysis performed on leachate

One of the chemical analyses carried out on the leachate was the total organic carbon (TOC). Therefore, the respective leachate results are presented in table 4.3, according to the concentration of NaOH and the duration of the treatment to which the RH was submitted.

Table 4.3 - Results of TOC analyses applied to the various leachate.

NaOH/Duration	TOC (mg/l)
0% - 2h	60,00
3% - 2h	80,00
6% - 1h	75,00
6% - 2h	85,00
6% - 4h	84,00
9% - 2h	130,00

First of all, it is important to note that TOC is a parameter that evaluates the organic matter (including sugars) released by the RH during the various treatment periods. As explained in subchapter 3.2, the higher amount of sugars and other harmful products released from the RH during treatment, the more beneficial it will be for cementitious mixtures.

The results shown in table 4.3 show that the increase in the parameter under analysis is proportional to the increase in NaOH concentration. In terms of the increase of the treatment period, it is beneficial to move from 1h to 2h of immersion. However, when it is increased to 4h, it becomes even harmful.

4.5 Resistance obtained at 28 days for the pastes produced

After knowing the results of the chemical analyses carried out on TOC, it is now important to understand the influence that the respective leachates have on the resistance of the pastes produced. In this context, the results of flexural and compressive strength, obtained at 28 days for the pastes produced, are presented in figure 4.2.

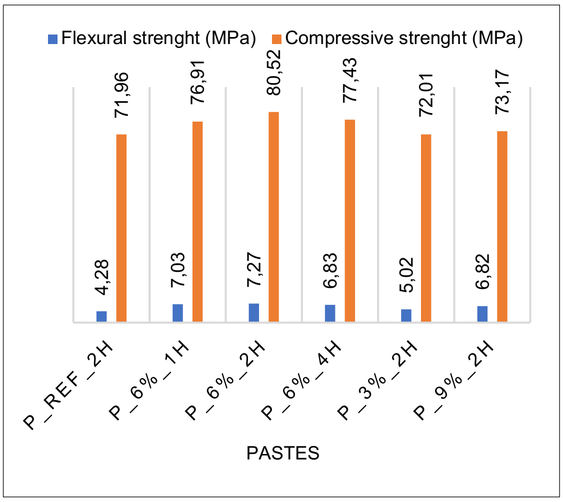


Figure 4.2 - Results of flexural and compressive strength, achieved at 28 days for the pastes produced.

Through the analysis of figure 4.2, it can be concluded that regardless of NaOH's concentration, leaches in the production of the pastes resulting from the treatment of RH leads to more beneficial results and higher flexural and compressive strength. To quantify the gains registered, for the paste P_6%_2h, were obtained increases of 70% and 12% in flexural and compressive strength, respectively.

4.6 Resistance obtained at 28 days for the mortars produced

As happened for the pastes, the alkaline treatment application to the RH permitted all the resistances to increase compared to the results obtained for the reference mortar M_Ref_2h. As expected, and since the RH characterization tests predicted these results, the NaOH concentration and treatment period's increase considerably benefits the composites produced, as shown in figure 4.3.

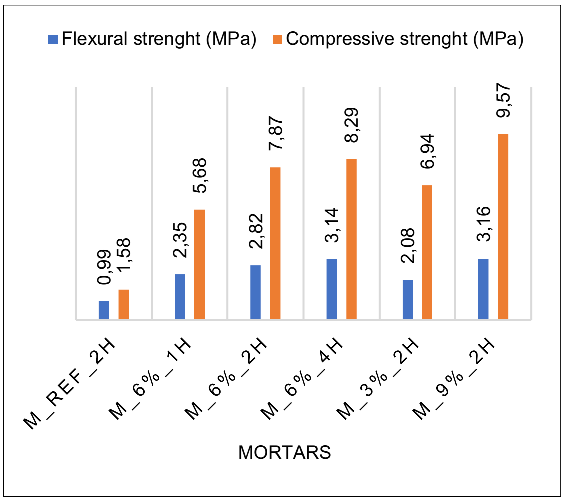


Figure 4.3 - Results of flexural and compressive strength, achieved at 90 days for the mortars produced.

In this context, it only remains to quantify the gains achieved, according to the reference mortar. The increases in flexural strength for the most resistant mixtures, M_6%_4h, and M_9%_2h, were approximately 220%, which is quite satisfactory. Concerning the compressive strength results obtained and using M_9%_2h mortar as an example, increases of approximately 510% were registered, which results in impressive gains of about 9 MPa.

Finally, it is possible to conclude that applying the treatment under study allows improvements in the mechanical interaction between the rice husk and the cement matrix, contributing to a better interfacial bond [9].

4.7 Resistance obtained at 90 days for the mortars produced

After presenting the main results at 28 days, it is now important to evaluate how mortars react to time evolution. In this context, figure 4.4 shows the flexural and compressive strength obtained at 90 days for the mortars produced.

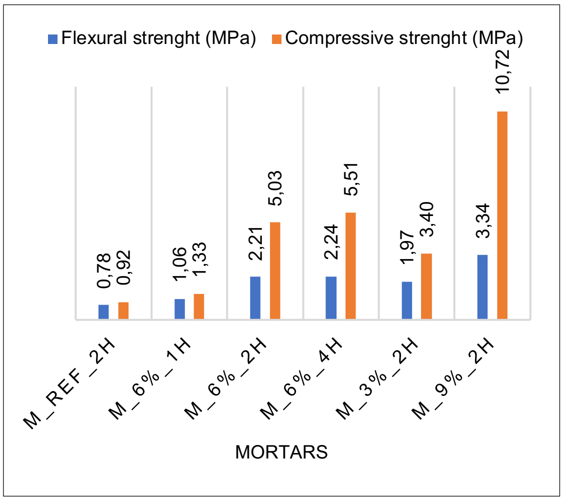


Figure 4.4 - Results of flexural and compressive strength, achieved at 90 days for the mortars produced.

The main highlight of the results presented goes to the registered breaks of both resistances in the transition from 28 to 90 days, except mortar M_9%_2h. The possible justification for this break may be related to the fact that during the first 28 days, the increase in resistance generated by the cement hydration process overlaps the micro-cracking, resulting from the shrinking effect of the paste and the RH. After this period, the cement's hydration stabilizes, which makes the retraction effect dominant, causing a loss of operability at the husk-paste interface and consequently a break in the mechanical resistances.

As concluded through table 4.1, the increased concentration of NaOH allows to reach better levels of workability and consequently a reduction of porosity. Therefore, as the NaOH concentration and the respective treatment period increase, the breaking effect on resistance is attenuated and even reverted to the M_9%_2h mortar.

Finally, it only remains to quantify the gains recorded. When comparing the results obtained for mortars M_Ref_2h and M_9%_2h, gains in the order of 1000% (9.94MPa) in compression and approximately 330% (2.56) in flexure were recorded. These results prove the positive effect that alkaline treatment produces on RH

4.8 Evolution of porosity over time

The evolution of the level of porosity over time provides a better understanding of the breaks in resistance recorded in the transition from 28 to 90 days. In this context and before any analysis, the results achieved in the open porosity test, recorded for each age, are presented in figure 4.5.

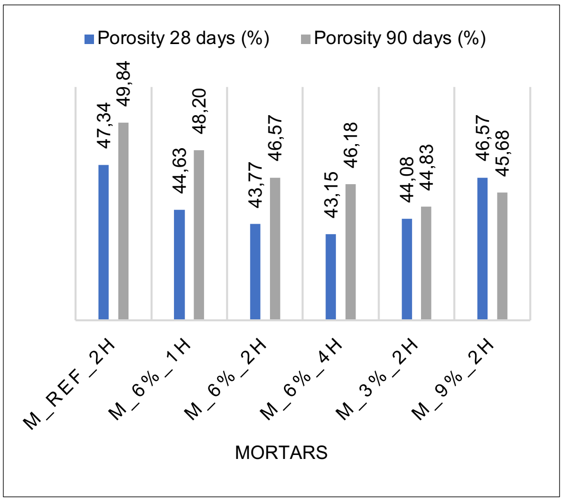


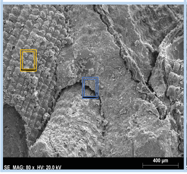
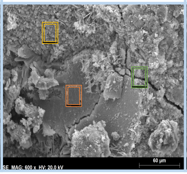
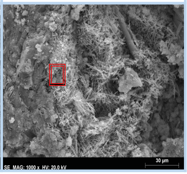
Figure 4.5 - Results of open porosity test, achieved at 28 and 90 days for the mortars produced.

First of all, it is important to note that porosity and mechanical resistance vary inversely. The higher the number of voids present in the mortars, the less they will resist certain loads. Therefore, the results obtained in the open porosity test confirm the resistance decreases observed, since excluding the mortar M_9%_2h, which suffered a decrease in porosity, all the others suffered an increase in the parameter under analysis. The increase in porosity is related to the above-mentioned micro-cracking phenomenon, resulting from the paste and the RH's shrinkage.

4.9 SEM test applied to mortars

This test's main objective was to evaluate the husk-paste interface to analyse how RH interacts with the cement matrix. In this context, the images captured for the different scales are presented in table 4.4.

Table 4.4 – Images captured during the SEM test, for the mortar sample observed.

M_6%_2h		
80x	600x	1000x
		

Through the first image captured on a scale of 80x, it is possible to see that the mortars have a cavernous structure, reflecting how the RH (yellow tag) is involved with the cementitious mixture (blue tag). In the second image captured at 600x, there are some cracking signs (green tag) in the cement matrix, resulting from the retraction effect previously discussed. There are also some calcium hydroxide lamellae developed along the cement hydration process (orange tag). In the third and last image, derived from the increase of the scale to 1000x, some needles of ettringites were developed at the beginning of the cement hydration process (red tag).

4.10 Susceptibility of mortars to water

This test was performed to evaluate the capacity of mortars and their constituents to resist successive drying/wetting cycles to understand if there were signs of mass losses or segregation with the evolution of time.

Therefore, the compressive strengths obtained for mortars at 28 and 90 days after this test are shown in figures 4.6 and 4.7, respectively. The compressive strength previously obtained for each age will also be presented in the same figures to quantify the breaks recorded, if any.

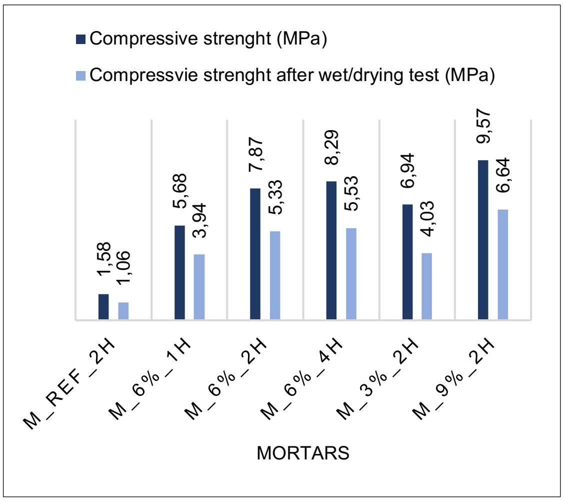


Figure 4.6 - Results of flexural and compressive strength, achieved at 28 days after wet/dying test.

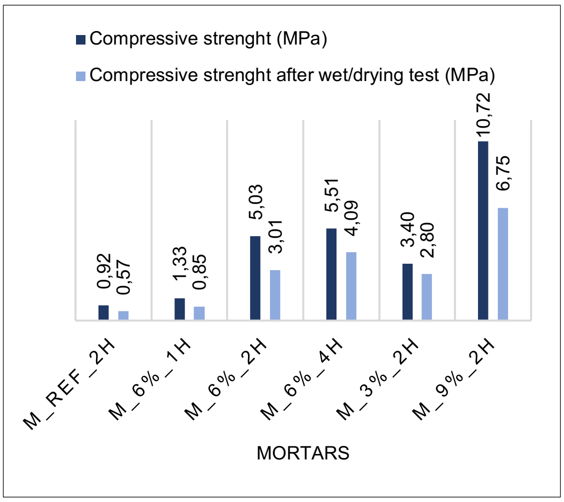


Figure 4.7 - Results of flexural and compressive strength, achieved at 90 days after wet/dying test.

Based on the results of both ages, the first conclusion is that there has been a break-in compressive strength after the mortars have been subjected to six drying/wetting cycles. This phenomenon can be justified because, during the various drying/wetting cycles, micro-cracks appear at the husk/paste interface due to the successive transitions from dry to saturated state. Concerning the results obtained at 28 days, the breaks registered were around 30% to 40%, while at 90 days, the breaks ranged from 20% to 40%.

Finally, the positive influence that alkaline treatment has on the RH must be reinforced once again. The compounds produced with treated husk present higher resistance and consequently offer more durability.

5 Conclusions

5.1 Final conclusions

The first major conclusion that can be reached is that the main objective of this study has been achieved as it has been proved that the application of the alkaline treatment and consequently the use of sodium hydroxide (NaOH), has considerably improved the less positive characteristics that the rice husk (RH) offers. Another conclusion drawn from the results achieved is that the intensification of treatment is positive for RH and its composites. It should also be noted that the treatment is more influential at the interface husk-paste and that this increase in intensity results in large improvements in adhesion and interconnection between RH and the cement matrix. Secondly, and since the incorporation of the RH in the mortars was not intended to serve as a reinforcement but to act as a light aggregate, it is concluded that the ideal mixture considers the cost/benefit ratio A_6%_2h. The previous choice's main reasons are that this mixture offers significant improvements compared to the reference mixture for this type of application and, the improvements noted for the RH mixture treated with 9% NaOH do not justify the increased investment in NaOH acquisition.

Finally, it only remains to be said that both RH and other vegetable fibers can reach interesting levels of performance, becoming in the short term a valid option in the engineering market, contributing to the reduction of negative impacts caused by the construction sector.

5.2 Suggestions for future studies

To end this study, it should be provided some suggestions for future studies, to continue all the work done.

The first suggestion is related to the fact that the optimum concentration of NaOH to be used has not been specifically determined. When considering the environmental impact, the increased cost of the treatment, and the decrease in thermal/acoustic performance, probably, and taking into account the purpose of the composites produced, it is concluded that intensification of the treatment is not the best option. In this context it is suggested that for a future study, a thermal/acoustic evaluation as well as a life cycle analysis should be performed, in order to conclude the optimal concentration of NaOH. The second suggestion is to develop an experimental campaign similar to the one considered in this study but applying a different treatment and reagent to the RH. In this context, it is suggested to apply a mineralization treatment using sodium silicate to the RH since it is considered to reduce its capacity to absorb water, increase its durability and resistance, and reduce its susceptibility changes in volume and shrinkage [14].

6 References

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