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# Combined Use of Ladle Furnace Slag and Rice Husk Ash as a Supplementary Cementitious Material

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Ladle Furnace Slag (LFS) is a solid waste from steel production that can be used in civil construction due to its high content of calcium oxides (> 50% CaO), contributing to the sustainability of both industries. Seeking to study its function as a supplementary cementitious material, the objective of this work was to determine the properties of coating mortars with the replacement of Portland Cement (PC) by 30% LFS combined with the pozzolanic effect of Rice Husk Ash (RHA). Prismatic specimens were produced in a 1:6 mixture proportion (PC:sand) and subjected to mechanical tests and determination of the dynamic modulus of elasticity. The results indicated that the replacement provided a reduction in mechanical strength, however the presence of LFS+RHA was beneficial to improve water retention. These changes were caused by the bigger surface area of RHA grains and the higher CaO content, in relation to the reference mixture.

**Keywords:** *industrial waste, binder, portland cement, mortar, sustainable construction*

## 1. Introduction

The civil construction industry has dedicated itself to reducing its environmental impacts, and one of the solutions found is the use of waste from other productive sectors as raw material, including waste generated by the steel industry[1,2]. Included in this context are the slags generated during steel production, with emphasis on Ladle Furnace Slag (LFS), with an estimated world production of 30 million tons per year[3]. Searches of the application of LFS in civil construction analyzed its use as an aggregate in cementitious matrices[4] and more recently as a Supplementary Cementitious Material (SCM) as an alternative to Portland Cement (PC)[5,6]. In the search for a binder with a more sustainable composition, this type of insertion makes it possible to develop products that reduce carbon dioxide emissions, energy consumption, waste disposal and the use of natural resources[7].

Based on this, LFS utilization has been investigated in order to improve the potential of this material, taking advantage of its chemical composition (high content of calcium oxides and hydroxides), transforming this residue into a co-product[8,9]. Its physicochemical properties are mostly influenced by the scrap used in steel production and by the cooling method adopted in the steel unit, as well[10,11], which also affects its chemical composition and granulometry, which can determine the performance of LFS as a binder[12]. So, monitoring free CaO and MgO contents is essential to control possible chemical reactions expansive[11]. Furthermore, the presence of 15 to 20% of amorphous material presented in the material favors this use[13,14].

This incorporation of LFS as SCM does not bring significant differences in essential properties such as anchoring capacity and dynamic modulus of elasticity in relation to mortars without slag[6,15]. Even with an increase in the water/binder ratio, these properties can be maintained, with proper choice of batch and dosage of the LFS[16]. However, chemical expansion may still be a cause for concern, as some studies have shown elevated values at 28 days, leading off a search for methods to mitigate the presence of chemical compounds that trigger volumetric instability. A useful way may be its combination with the use of siliceous materials that may favor the formation of C-S-H by the consumption of CaO[6,9].

In this way, the incorporation of a pozzolana is a favorable method to enhance the LFS use as binder, considering that this type of slag has a high content of calcium hydroxide, an essential compound for pozzolanic reactions[7,11]. Among this type of materials, Rice Husk Ash (RHA) stands out as a viable alternative due to its satisfactory reactivity from non-crystalline silica[17,18]. RHA is already utilized as a pozzolanic addition, with positive results in terms of mechanical properties and durability, in addition to environmental benefits[19,20]. It has been observed that the pozzolanic reaction converts portlandite with amorphous silica into C-S-H phases, which may lead to a higher content of portlandite in early ages. On the cementitious microstructure, its effect has brought better results in terms of durability and compressive strength,

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resulting from the pronounced dense microstructure, which in turn greatly reduced the absorption of capillary water in the specimens[21]. Positive results were also seen in the use of a controlled batch of RHA, which potentiated the pozzolanic reaction and improved durability and resistance properties, with an improvement in specific and long-term compressive strength, greater ductility under compressive load, in addition to shrinkage rates per drying like the control, ensuring tightness[22].

Therefore, the objective of this work was to determine the mechanical properties of cementitious mortars with 30% replacement of Portland Cement (PC) by LFS and addition of 10% of RHA, as a supplementary cementitious material.

## 2. Materials and Methods

The LFS sample was provided by a company in the steel sector, located in the Piracicaba/SP region, defined according to the type of cooling and texture (by air and fine, respectively), compatible with the objective of this research (replacement part for Portland Cement by LFS). Portland cement (CP II-F), rice husk ash (RHA), quartz sand (QS) and local water supply were also used as materials in the research. To carry out the tests, the sample was dried in an oven at 105 °C and cooled to room temperature. To increase its fineness, a pre-processing with sieving and grinding in a ball mill was carried out, using the material that passes through the sieve with an opening of 0.6 mm[23], as in Figure 1.

Next, the methodology of this research was divided into two stages: physical-chemical materials characterization and the determination of the mortar mechanical properties. The characterization of the materials was carried out through tests to obtain the water content[24], specific mass[25], and laser granulometry, in addition to X-Ray Fluorescence (XRF), and Loss on Ignition (LOI) analysis.

For the mortar study, the replacement content of PC by LFS was set at 30% based on the study by Silva[26], who evaluated the same batch of slag, while the RHA index was 10%, also according previous literature[17]. The mix proportions were defined for coating mortar and based on similar previous research[6,8] and the water/binder ratio was defined according to the Flow Table tests[27], considering a normal consistency of 260 mm (± 5 mm). Table 1 details the mixture proportions and respective identifications.

To determine mortar properties, still in the fresh state, water retention and density tests were also carried out, according to NBR 13277[28] and NBR 13278[29], respectively. Regarding the properties in the hardened state, tests were carried out to determine the bending tensile strength ($Ts_m$), compression strength ($Cs_m$)[30], dynamic modulus of elasticity ($E_d$)[31], density[32] and water absorption by capillarity[33]. In view of the analysis of the results, obtained the classification of mortars according to NBR 13281[34].

## 3. Results and Discussion

Figure 2 shows the granulometric curves of the LFS after pre-processing, the RHA and the PC. The fineness results of the samples show that the sieving benefited the LFS because, by making the material thinner, it increases its specific surface, favoring hydration reactions[23].

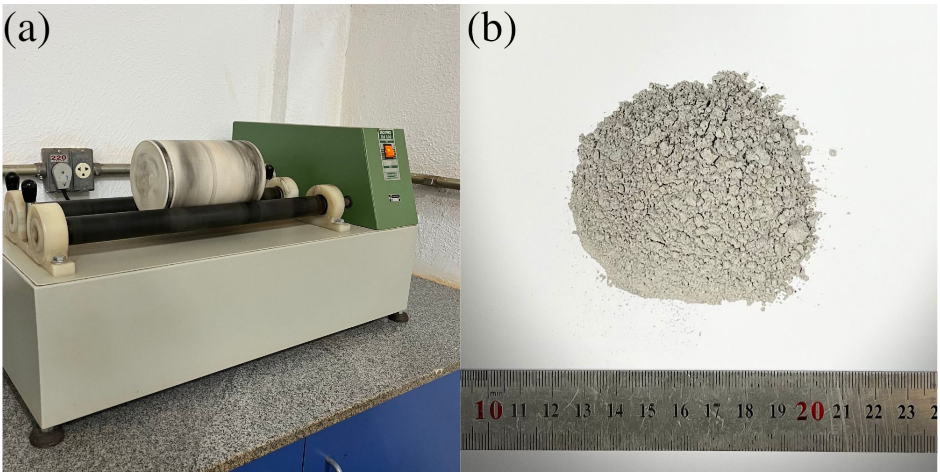


**Figure 1.** (a) Pre-processing of the LFS sample using MA500 ball mill with alumina ceramic jar and (b) LFS after pre-processing.

**Table 1.** Volume proportions of mortar mixtures.

| Identification | Binder | | | Aggregate |
|---|---|---|---|---|
| | PC | LFS | RHA | Sand |
| REF | 1.0 | 0.0 | 0.0 | 6.0 |
| REF-RHA | 0.9 | 0.0 | 0.1 | 6.0 |
| LFS | 0.7 | 0.3 | 0.0 | 6.0 |
| LFS-RHA | 0.6 | 0.3 | 0.1 | 6.0 |

**Table 2.** Chemical composition of materials samples.

| Sample | Chemical elements (%) | | | | | | | | | | | LOI (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CaO | $SiO_2$ | MgO | $Fe_2O_3$ | MnO | $SO_3$ | Si | K | Ca | Al | Mn | |
| LFS | 54.6 | 9.78 | 5.79 | 7.59 | 7.29 | - | - | - | - | - | - | 12.0 |
| RHA | - | - | - | - | - | - | 88.94 | 5.97 | 1.66 | 1.33 | 1.15 | - |
| CPII-F | 63.4 | 12.4 | 2.83 | 3.86 | - | 2.76 | - | - | - | - | - | 10.8 |

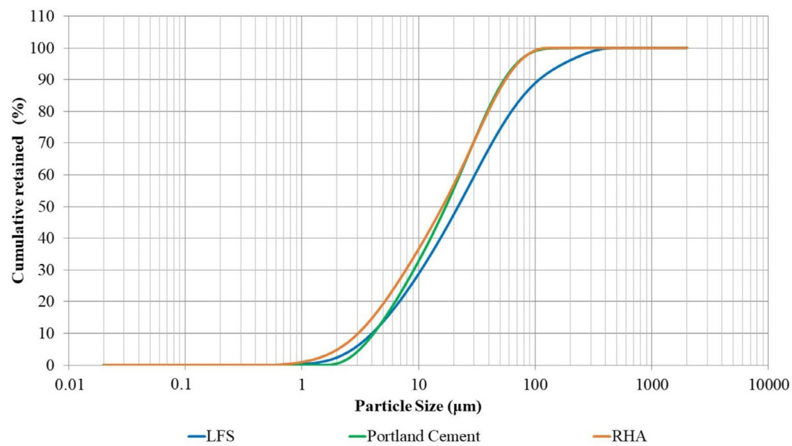


**Figure 2.** Granulometric curves of PC II – F, LFS and RHA samples.

The LFS sample also demonstrates similarity with the PC, presenting very close values for D10 in relation to Portland cement (PC II-F), a characteristic strongly influenced by the slow cooling method adopted[10]. The greatest difference occurs in the mean diameter of the LFS (44.6 µm) in relation to that obtained for the PC (25.15 µm), which can be adjusted during slag processing (grinding and sieving).

Regarding the materials density, the sand sample presented a value of 2.65 g/cm$^3$, while PC and LFS demonstrated results of 3.00 g/cm$^3$ and 2.70 g/cm$^3$, respectively. Being slightly lower than the PC result, the LFS density is another property influenced by the reactions in the sample cooling process[6,8], where the binding properties of the residue were also determined[10,11,26].

The RHA, on the other hand, presented a significantly lower density (2.05 g/cm$^3$). For the chemical characterization, the XRF and LOI tests were carried out, which results are shown in Table 2. It can be seen that the LFS and PC samples have a high CaO content (55% and 63%, respectively), as well as other chemical elements, also important to obtain hydraulic chemical reactions ($FeO_2$; $SiO_2$), however, in different levels. The amount of free lime in the LFS is adequate when observing better hydration and controlled of the chemical reactions expansion when used in cementitious matrices[6,13]. $FeO_2$ and $SiO_2$ contents varied in relation to PC and are relevant since they are correlated with the hydraulic reactivity potential of LFS, especially between silica and possible volumetric instabilities[8].

The XRF analysis (Table 2) showed that the main oxides present in the LFS sample are CaO, $SiO_2$, $Fe_2O_3$, MgO, MnO. Through XRD analysis (Figure 3), it was possible

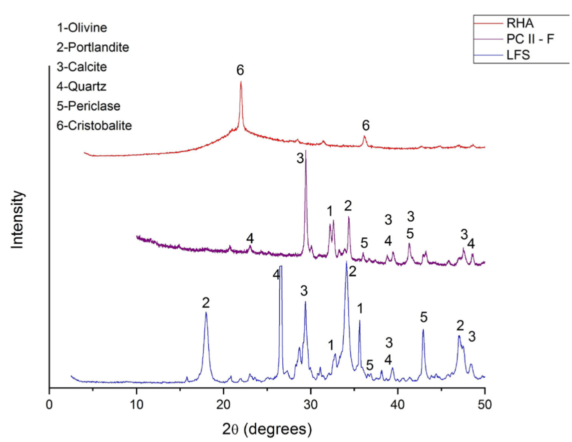


**Figure 3.** Main peaks of compounds presented in the XRD analysis of the materials.

to verify the combined formation of olivine, portlandite, calcite, quartz, periclase, which are also present in the PC sample and in other studied LFS samples[11,35]. These results endorse the sample's potential for use as a SCM, as they demonstrate a composition that leads to the formation of C-S-H in cementitious matrices during the hydration process[6]. Meanwhile, the RHA diffractogram exhibited a cristobalite ($SiO_2$) peak.

The images obtained by Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM+EDS) allowed obtaining the morphology of the slag particles and identifying the main chemical compounds (Figure 4).

In addition, the images demonstrated that the particle shapes of this LFS sample are different, due to the pre-processing performed. The EDS analysis identified the elements: O, Ca, Mn, Fe, Mg and Si, like the sample studied by Henríquez et al.[35], when the presence of the same compounds was observed, with the addition of aluminum oxide. The occurrence of this element in the LFS is associated with the addition of aluminum during the deoxidation process of the secondary refining of steel in the ladle furnace[6].

According the characterization results of mortars in the fresh state displayed in Table 3, an increase in the water/binder ratio of mortars with LFS (1.62) and LFS+RHA (1.95) is observed in relation to the reference (1.13), making up 43% and 72% respectively. This raise is justified by the bigger surface area of the RHA grains and the higher CaO and $Ca(OH)_2$ content in the LFS (chemical elements that have a greater capacity for absorbing and retaining water). As a result, there were larger spreading taxes of mortars with LFS and with RHA, improving their workability. In time, Herrero et al.[36] also studied the properties of mortars with LFS (35% replacement of PC), reporting similar behavior. Still on the properties in the fresh state, only mortar with LFS+RHA consumed the minimum value of 79% in relation to water retention, as required by NBR 13281[34], inferring that the presence of LFS significantly improved with the mortars studied, in relation to the fresh state of the reference mortar.

Table 4 presents the results of the mortars in the hardened state, also showing the statistical analysis of the results by the ANOVA method and comparison of means by the Fisher Test. Regarding $Ts_m$ and $E_d$, it appears that REF+RHA and REF are statistically equal, as well as EFP+RHA and LFS. These two properties are crucial in the study of coating mortars as they reflect, respectively, their anchoring capacity and ability to absorb deformations when acting in a constructive system[6,8].

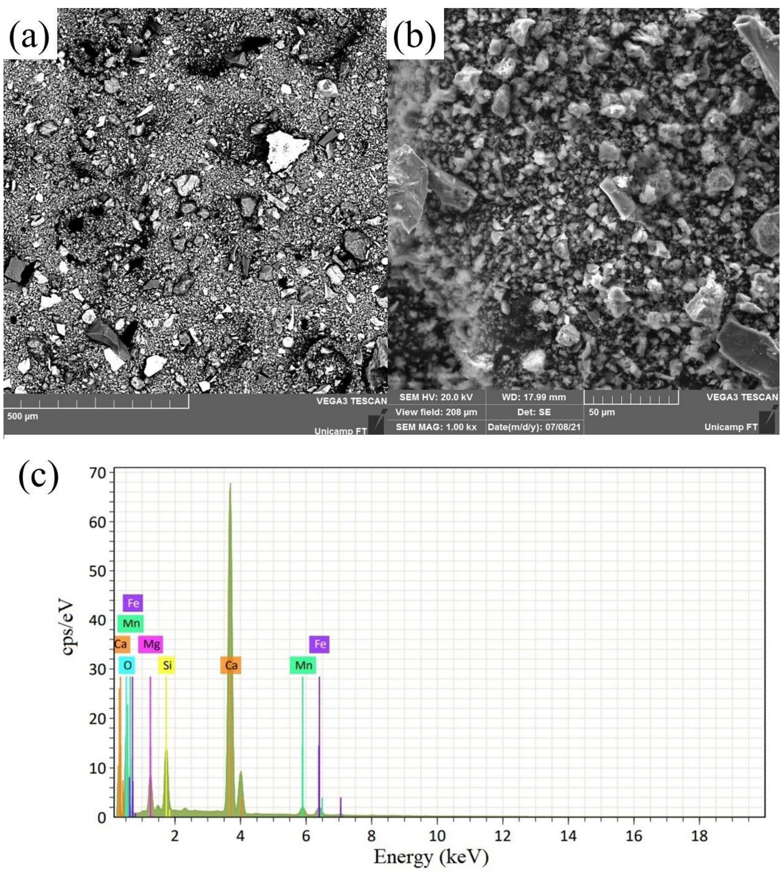


**Figure 4.** SEM images of LFS sample in (a) 200x and (b) 1000x magnitudes, and (c) EDS spectrum showing relative intensities of LFS chemical elements.

**Table 3.** Properties analysis of mortars in the fresh state.

| Property | REF | REF+RHA | LFS | LFS+RHA |
|---|---|---|---|---|
| Consistency index (mm) | 257 | 258 | 260 | 262 |
| Water binder ratio w/b | 1.13 | 1.26 | 1.62 | 1.95 |
| Water Retention (%) | 74 | 77 | 63 | 79 |
| Density ($kg/m^3$) | 2,158 | 2,153 | 2,138 | 2,174 |

**Table 4.** Properties analysis of the mechanical properties of mortars.

| Property | REF | REF+RHA | LFS | LFS+RHA |
|---|---|---|---|---|
| $Ts_m$ (MPa) | 1.82 | 1.84 | 1.48 | 1.14 |
| SD (MPa) | 0.09 | 0.04 | 0.07 | 0.16 |
| CV (MPa) | 0.05 | 0.02 | 0.05 | 0.011 |
| P-value | | 0.00121 | | |
| Homogeneous Groups | A | A | B | B |
| Class | R2 | R2 | R2 | R2 |
| $Cs_m$ (MPa) | 6.81 | 6.19 | 4.66 | 4.13 |
| SD (MPa) | 0.45 | 0.23 | 0.17 | 0.19 |
| CV (MPa) | 0.07 | 0.04 | 0.04 | 0.05 |
| P-value | | $7.33e^{-13}$ | | |
| Homogeneous Groups | A | B | C | D |
| Class | P5 | P4 | P4 | P4 |
| $E_d$ (GPa) | 13 | 12 | 9 | 8 |
| SD (GPa) | 0.58 | 0.57 | 0.29 | 0.49 |
| CV (GPa) | | | | |
| P-value | | $4.24e^{-6}$ | | |
| Homogeneous Groups | A | A | B | B |

SD: Standard deviation; CV: coefficient of variation.

It was possible to state that the presence of RHA did not change the mortars behavior, that is, the expected effect of mechanical resistance increase did not occur. This process took place due to the short curing period (28 days) which is not enough for complete pozzolanic chemical reactions. By comparing the results of the mortars with LFS and RHA with the REF mix, it is verified significantly reduced the values of $Ts_m$, $Cs_m$, and $E_d$, same behavior was observed with 45 days interval[36]. In this sense, is worthy to mention that the reduction of the mechanical properties of mortars with LFS is caused by the average diameter of its particles, as well as by the lower percentage of amorphous chemical compounds. As for $E_d$, the decrease can be considered beneficial for the coating mortars, as the LFS reduced the stiffness of the mortars studied. Altering this property favors the absorption of tensions resulting from deformation and accommodation (shrinkage, movement of masonry, thermal variations in the environment).

The mortar classification according to NBR 13281[34] indicates that the mixtures with LFS showed the same behavior as the REF mix, when considering $Ts_m$ results, all classified as R2. However, the same did not happen for compressive strength, when REF was classified as P5, while the other mixes were in P4 class. This property was more affected at 28 days by the incompleteness of hydration reactions; however, it may have a slight recovery at higher ages due to the slow release of water in the matrix, making it available to react with unreacted components of LFS[37].

The capillarity coefficient test presented the following results: 4.38, 5.79, 8.95, and 9.35 for the REF, REF+RHA, LFS, and LFS+RHA mix groups, respectively. By this, they were classified as C4 for mixtures without LFS and C5 for mixtures with LFS[34]. These changes in compressive strength and capillarity coefficient are explained by the increase in the w/b ratio in mortars with LFS, triggering a decrease in mechanical strength. Nevertheless, this does not necessarily represent a loss in the performance of the matrix, since mortars for coating walls are more requested regarding support and absorb deformations, which require less rigidity, that is, less mechanical strength[38,39]. In this sense, $E_d$ is also an important parameter to assess the range of absorption of deformations between the substrate and the mortar, which occur during the drying and hydration cycles, in addition to the established importance in the demands of the structure in service[6,38,40].

## 4. Conclusions

In view of the proposed objective, it was demonstrated that the use of LFS as a complementary binder in the partial replacement of PC (30%) and addition 10% RHA does not affect the behavior of mortars the fresh state. However, changes in the hardened state resulted in changes in relation to classification, according to NBR 13281[34]. But, the lower values in the compressive strength and capillarity coefficient, can be evaluated as beneficial as it reduced the stiffness of the mortars, contributing to the reduction of shrinkage and deformation cracks. As reasons for changes in the mechanical properties of mortars with LFS and LFS+RHA, are cited: the average diameter of the slag greater than that of PC, chemical composition, and insufficient curing period for the expected pozzolanic chemical reactions.

For the next studies, it is indicated to study the behavior of mortars aged over 28 days, for a better evaluation of pozzolanic reactions.

## 5. Acknowledgments

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