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## The effect of calcination conditions on oat husk ash pozzolanic activity

A.L. Bonifacio\*, P. Archbold

Sustainable Infrastructure Research Group, Technological University of the Shannon: Midlands Midwest, Athlone N37HD68, Ireland

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## ABSTRACT

Supplementary cementitious materials (SCMs) are known and used to reduce cement consumption, but some waste sources currently used for partial cement replacement are threatened by changing industrial production processes and local availability. Thus, considering possible sources of amorphous silica for use as SCM, especially pozzolans, there is an opportunity to investigate the use of agricultural residues such as oat husks, which currently have little or no commercial value. This work aims (i) to identify the burning temperature that promotes the reduction of carbon content and increase the amorphous material, (ii) to present the chemical and physical characterization analysis results, and (iii) to evaluate the pozzolanic potential of selected oats husks ashes (OHA) produced under controlled calcination temperatures. Local samples of oat husks were sun-dried, sieved, and split into two portions. One portion was subjected to analysis of moisture content, and the second portion was pre-calcined at 350 °C for 2 h in an aerated laboratory oven and turned into ashes under 400 to 700 °C respectively, using ramp heating rate of 10 °C/min. The ashes were ground in a ball mill and subjected to chemical and physical analysis, considering Loss on Ignition (LOI) at 950 °C, chemical composition through Energy Dispersive X-Ray Analysis (EDX), structural state analysis by X-ray diffraction (XRD), morphology by digital microscopy, density using glass pycnometer and chemical reactivity with calcium hydroxide measured through thermogravimetric analysis of a control mortar defined as (R<sup>3</sup>) model paste. The results show that the ash chosen for pozzolanic potential analysis, produced at 600 °C, shows an average ash content value of 3.6%, and chemical concentration of 45.97% oxygen (O), 21.2% silicon (Si), and 16.91% potassium (P), in addition to evidence that characterizes crystallization of its structure and consumption of 8.74% of Ca(OH)<sub>2</sub> from the control matrix, indicating low pozzolanic activity. It was concluded that local oat husks in Ireland calcinated between 600 and 700 °C presented a favorable balance between the percentage of residual carbon amount and silica in the amorphous form that is favorable to react with calcium hydroxide forming calcium silicate hydrate. It opens up a possibility of investigating the use of OHA as SCM, requiring more studies about the oats husks calcination time, cement replacement rate, and performance tests to consider practical applications, and maybe contributing to reducing the OPC consumption, production necessity, and consequently, the environmental issue caused by its production.

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## 1. Introduction

Cement is one of the most consumed materials on the planet, accounting for 4.1 billion tons [1] produced and 7% of worldwide carbon dioxide (CO<sub>2</sub>) emissions in 2019 [2]. The major environmental challenge in cement production is that the chemical decomposition process to manufacture the main part of its composition, called clinker, emits 60–70% of the CO<sub>2</sub> produced in the pro-

cessing phase [2], reaching approximately 840 kg per ton of clinker produced [3]. To alleviate the need for clinker production, strategies such as partial replacement of cement by supplementary cementitious materials (SCMs) are being applied, and new sources investigated [4]. The supplementary cementitious materials (SCMs) are fine powders that can be found in, siliceous, aluminosiliceous, or calcium aluminosiliceous forms [4], classified as inert and used as fillers materials or reactive as in the case of pozzolans, which naturally do not have cementitious properties [5], but when combined with Portland cement obtains through the cement hydration process the remaining calcium hydroxide [Ca(OH)<sub>2</sub>], popularly

\* Corresponding author.

E-mail address: [alyssonlarsen@gmail.com](mailto:alyssonlarsen@gmail.com) (A.L. Bonifacio).<https://doi.org/10.1016/j.matpr.2022.03.197>

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known as hydrated lime, necessary to react with amorphous silicon dioxide ( $\text{SiO}_2$ ) present in pozzolanas to create more calcium-silicate hydrate (C-S-H) binder through a secondary reaction called pozzolanic reaction [6].

Because some plants polymerize amorphous silica in their cells, particularly in the palea and lemma, generally referred to as the husk or hull [7], which is transformed into reactive silica after a controlled combustion process, to obtain a rich silica skeleton as product [8]; Some low-cost, renewable, and high availability resources such as agricultural biomass have been studied as SCMs, primarily as siliceous pozzolans [9]. Land plants have a high capacity to accumulate silica, particularly in the Gramineae (Poaceae) family, which includes many species cultivated in modern agriculture [10], where rice husks stand out in the engineering field, having calcination parameters investigated in terms of temperature, retention time, and cooling and heating rate to obtain the highest concentration of highly reactive silica [8].

In the current scenario, the investigation for new viable sources of SCMs is justified, as the production of commercial SCMs, such as granulated blast furnace slag and fly ash used in the production of blended cements, is threatened by the future unavailability of these materials [2], since the heating, power generation, and metal processing systems, from which these by-products originate, foresees a change in the production strategy to less polluting production methods [11], reducing or eliminating their generation. Because the ability of plants to accumulate  $\text{SiO}_2$ , and the existing studies about the use of rice husks as sources of silica, there is the possibility of investigating oats (*Avena sativa* L.), the third most cultivated cereal in Ireland, whose the great majority are husked oats [11]. The great majority of oat husks are separated from the grains in mills and do not have a well-defined destination, being used in the production of energy for small users, as filter bed in the artisanal production of beverages, as animal feed, decomposed for fertilizer production, buried to enrich the soil or considered a waste material with little commercial value [12].

Considering that rice and oat husks belong to the same family and present the same structures where the largest portion of silica is concentrated, theoretically, ashes of local oat husks calcined at controlled specific temperatures, when in a fine powder form with a minimum dimension of  $45\ \mu\text{m}$  to comprise the ASTM C618-05 Standard [13] particle size requirement, present characteristics and sufficient amorphous silica to react with  $\text{Ca}(\text{OH})_2$  and promote pozzolanic reactions. Thus, this article aims to investigate the temperature necessary to obtain the maximum possible concentration of highly reactive amorphous silica from OHA, using a controlled calcination process, chemical and physical investigations and the evaluation of the pozzolanicty of the material obtained.

## 2. Experimental program

### 2.1. Materials

#### 2.1.1. Oats husks

The oat husks (raw material) used were harvested in the region of Co. Wexford in the Republic of Ireland, supplied wet and without previous treatment by the company Millstream Recycling Ltd. in July 2020. The husks offered were derived from the food industry's process of dehulling oat grains, collected by the company, and sold as a source of fiber for animal feed. The material was transported to the study site in black polypropylene bags, washed in the laboratory using distilled water, sun-dried, and sieved to reduce impurities and traces of oats still attached to the husks. Following the drying and sieving process, the material was split into two portions. The structures that make up the oat husks used in this study

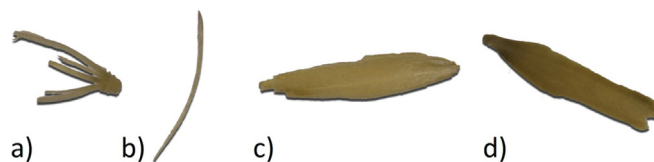


Fig. 1. (a) Glumes encounter; (b) Awn of Lemma; (c) Palea; (d) Lemma.

can be seen in Fig. 1, which are indicated in the literature as the plant region with the highest concentrations of silica [7].

#### 2.1.2. Chemical materials

To prepare the mixture suggested by Avet et al. [14], denominated  $R^3$  model paste, was used powder potassium sulphate ( $\text{K}_2\text{SO}_4$ )  $\geq 99\%$  purity, potassium hydroxide (KOH) pellets  $\geq 85\%$  purity, powder calcium carbonate ( $\text{CaCO}_3$ )  $\geq 99\%$  purity, powder calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ]  $\geq 95\%$  purity with less than 3 wt% of  $\text{CaCO}_3$ , and deionized water. The white microsilica type ZZ used as reference material for x-ray diffraction (XRD) analysis is commercial and, according to the producer, has 95.6%  $\text{SiO}_2$  and 2.6% Zirconium dioxide ( $\text{ZrO}_2$ ) in its composition.

### 2.2. Methods

The series of operations to which the oat husks were subjected is depicted in Fig. 2.

#### 2.2.1. Evaluation of the raw material moisture retention

To determine the ability of the raw material to retain moisture, husks from the first portion were dried for 24 h in an electric oven at  $105\ ^\circ\text{C}$ , cooled in a desiccator, and later weighed on a Benchtop scale PCE-BSK 310 with the resolution of 0.001 g. The dried husks were then left in the open air for 24 h and later weighed to perform the moisture analysis, evaluating the difference between the mass of material in the open air and material dried at  $105\ ^\circ\text{C}$ .

#### 2.2.2. Oats husk calcination process

To reduce the carbon content and avoid ignition, the second portion of husks was carbonized in a stainless steel pan with dimensions of 162 mm length, 176 mm width, and 100 height at  $350\ ^\circ\text{C}$  for 2 h in an aerated laboratory chamber furnace (Gero Carbolite CWF-B 1200) using a heating ramp of  $10\ ^\circ\text{C} / \text{min}$ . After the calcination, the temperature was raised using the same heating ramp until the desired temperatures range of  $400$  to  $700\ ^\circ\text{C}$  respectively, the most used temperature range reported in the literature in the production of ashes to pozzolanic potential investigation [7], and then the ashes were retained for more 2 h, being mixed with a stainless steel bar every 30 min.

#### 2.2.3. Ashes grinding and sieving

After the period of retention, the ashes were ground for 10 min sections in a laboratory ball mill (Planetary mono mill Pulverisette 6 classic line) using twelve balls of hardened stainless steel  $\varnothing 15\text{mm}$  considering previous biomass pozzolan studies [9] that point to greater pozzolanic effectiveness through increasing specific area. The ashes were ground until 70% of the ashes passed through a  $45\ \mu\text{m}$  sieve, meeting the ASTM C618 Standard requirements [13].

#### 2.2.4. Chemical analysis

To characterize the ashes and identify which ones have the most favorable characteristics to be considered pozzolanic according to the ASTM C618 Standard, the ground material was submitted to chemical and physical analysis, considering the loss on

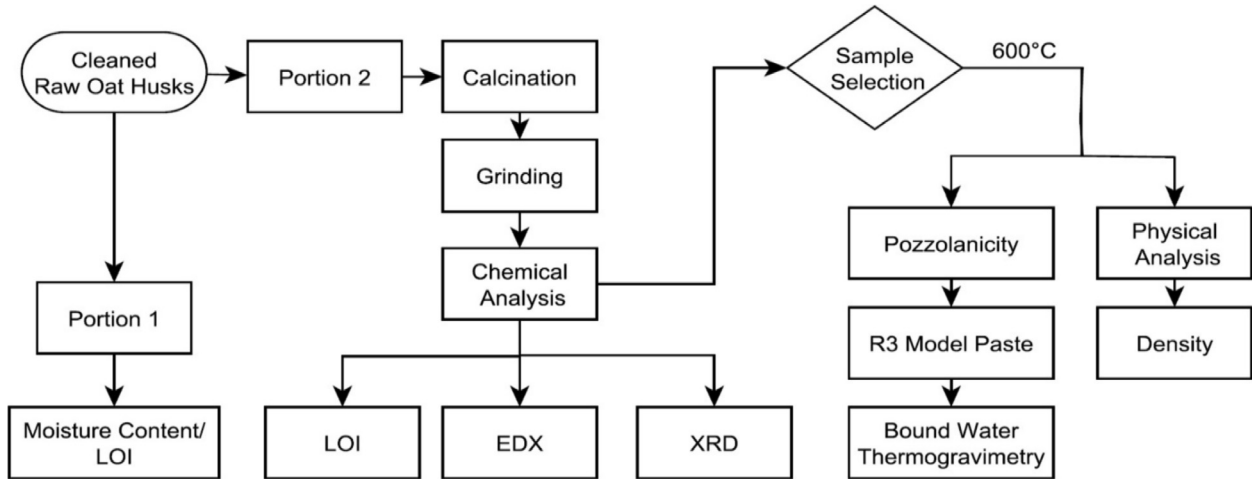


Fig. 2. Experiment workflow.

ignition at 950 °C (LOI950), the chemical composition of ash samples coated in gold by a sputter coater (Baltec SCD 005) using Energy Dispersive X-Ray Analysis (EDX) in an TESCAN MIRA scanning electron microscope, and the structural state of elements through x-ray diffraction (XRD) data from material scanned in a Bruker D2 Phaser with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at 30 kV, 10 mA using a zero background holder.

**2.2.4.1. Loss on ignition (LOI).** Loss on Ignition analysis is a test often used in mineral analysis, based on the igniting of a sample at defined temperatures in a reactive oxygen atmosphere, promoting oxidation and the release of volatiles [15]. The performed procedure consisted of the pre-ignition of alumina crucibles and a few grams of the sample at 105 °C (D105) for 24 h in an electric oven and drying in a desiccator, weighing of the dry and cooled set on a Benchtop scale PCE-BSK 310 with resolution of 0.001 g, followed by ignition of the samples in an aerated laboratory chamber furnace, in alumina crucibles at the desired temperature for 6 h, and weighing of the cooled set after ignition (Dfinal). The estimation of residual carbon expressed as a percentage is the result of the arithmetic mean of successive analyzes by calculating the difference of the dry material at 105 °C and after ignition, using Equation (1) [16].

$$LOI_{950} = \left( \frac{D_{105} - D_{final}}{D_{105}} \right) \times 100 \quad (1)$$

### 2.2.5. Physical analysis using the pycnometry

The relative density analysis of the selected ash was performed with the aid of a Benchtop scale PCE-BSK 310 and a standard 20 ml pycnometer, with its volume was verified (V) by filling it with water and dividing the used water mass value by the density of water ( $\gamma_w = 0.997 \text{ g/ml}$ ). The procedures for carrying out the samples density calculation according to Equation (2) started with successive measurements of pycnometer mass (Mini), the mass measurement of the pycnometer filled with a known quantity of sample (Msam), and with mass measurement of the set filled with water (Mwat).

$$\gamma_{oat} = \frac{Msam - Mini}{V - \left( \frac{Mwat - Msam}{\gamma_w} \right)} \quad (2)$$

### 2.2.6. Pozzolanicity

The chemical reactivity with calcium hydroxide was evaluated through its use for the synthesis of the R<sup>3</sup> model paste [14], to

assess SCM reactivity individually, without considering the influence of cement hydration. Thus, the R<sup>3</sup> Model paste with the selected ash was submitted to water-bound oven method analysis and thermogravimetry analysis (TGA).

**2.2.6.1. R<sup>3</sup> model paste synthesis.** An reference mortar (R<sup>3</sup> model paste) was produced using the recommendations suggested by Avet et al. [14], considering the proportions shown in Table 1 to test the ashes reactivity in a mixture of SCM and Ca(OH)<sub>2</sub>, replicating the circumstances of a cementum mixture. Initially, KOH and K<sub>2</sub>SO<sub>4</sub> were added in a glass beaker using a spatula and dissolved in deionized water at 40 °C with the help of a magnetic stirrer at 1600 rpm. The CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>, and ashes were homogenized and added to the solution, which was then stirred for 5 min at 1600 rpm until a homogenous paste was formed. The paste was then added to polypropylene bags and sealed taking care to remove all the air, and stored at 40 °C in an oven for 7 days.

**2.2.6.2. R<sup>3</sup> model paste bound water by oven method.** Pieces of the paste samples cured for 7 days were crushed by hand and placed inside alumina crucibles; the set (crucible + sample) was dried at 110 °C in an oven for 24 h, cooled in a desiccator, and weighed (m1). The dry set was then subjected to calcination in an aerated laboratory chamber furnace at 350 °C for 2 h, cooled in a desiccator, and its weight was then re-determined (m2). This method assumes that only the water inside the pores is removed up to 105 °C [17]. The bound water was calculated according to Equation (3) [14].

$$\text{Bound water}(\%) = 100 \times \left( \frac{m1 - m2}{m1} \right) \quad (3)$$

**2.2.6.3. R<sup>3</sup> model paste TGA analysis.** The paste samples, cured for 7 days, were crushed into small pieces, ground to pieces smaller than 4 mm, and stirred in isopropanol for 20 min to stop the hydration process. The material was separated from the suspension by vacuum filtration using filter paper, and the retained material was dried on a watch glass for 10 min in an oven at 40 °C. The TGA measurement was carried in an alumina crucible, and approximately 10.353 mg of samples were heated from 30° to 700 °C at 10 °C/min under a 20.0 ml/min nitrogen flow in a Pyris 1 TGA Thermogravimetric Analyzer. The data analysis was performed using specialized software (Pyris Software), and the mass loss between 400 and 480 °C was calculated using the tangential method proposed by Lothenbach et al. [17], considering the temperature range

**Table 1**  
R<sup>3</sup> model paste components.

Components	Ashes	KOH	K <sub>2</sub> SO <sub>4</sub>	Ca(OH) <sub>2</sub>	CaCO <sub>3</sub>	Deionized Water
Mass (g)	11.11	0.28	1.2	33.33	5.56	60

of 400–500 °C pointed to the dehydroxylation of calcium hydroxide [18]. The calculation of residual [Ca(OH)<sub>2</sub>] (mCH, residual) and consumed [Ca(OH)<sub>2</sub>] (mCH, consumed) was performed according to Equation (4) and Equation (5), an adaptation of the formula proposed by Lothenbach et al. [17].

$$mCH, residual \left( \frac{g}{100gSCM} \right) = \frac{\Delta mH_2O, CH \left( \frac{g}{100gSCM} \right) \times 18.02 \left( \frac{g}{mol} \right)}{74.09 \left( \frac{g}{mol} \right)} \quad (4)$$

$$mCH, consumed(g) = \frac{mCH, mix \left( \frac{g}{100gSCM} \right) - mCH, residual \left( \frac{g}{100gSCM} \right)}{100(g)} \quad (5)$$

### 3. Results and discussion

#### 3.1. Raw material moisture retention

When considering the different uses of lignocellulosic materials, especially those related to thermic transformation, it is important to recognize parameters related to the ability of these materials to absorb water in large quantities [19], considering that it is necessary to apply energy to process the material and considering that for RHA, its necessary a minimum of 402 °C to destroy the organic matter [20], even because oat husks have 25% lignocellulose in their composition [12]. The analysis of the moisture absorbed by the oat husks in the open air showed that the local oat husks absorbed an average of 6.14% of moisture in relation to their weight.

#### 3.2. Effects of burning temperature on the color of OHA

The oat husk calcination products produced under the temperature range of 400 to 700 °C, respectively, are shown in Fig. 3 as a coloring material that varies from black to gray tones based on the temperature used, similar results to those observed in the production of rice husk ashes (RHA) [6]. The black color of ash particles indicates the presence of carbon due to incomplete combustion [21], which may be better observed by examining the unground ashes through digital microscopy, as illustrated in Fig. 4.

The presence of carbon may be associated with an absence of sufficient oxygen for carbon oxidation [22], possibly caused by the formation of a surface layer that entrapped the carbon to the ash as a result of a quick temperature increase, causing the superficial fusion of potassium oxide (K<sub>2</sub>O) preventing particle contact

with air, as observed in RHA [21] and due to the fact that black spots are observed even under increasing temperature, illustrated in Fig. 4c.

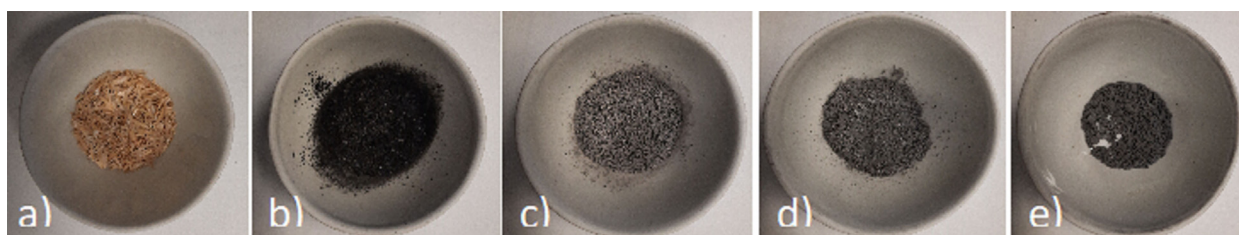
#### 3.3. Effects of burning temperature on the carbon content and chemical composition

One of the ASTM C618 conditions for a calcined material to be classified as natural pozzolan (Class N) is that the percentual achieved in the LOI analysis be less than 11%, and that the sum of Silicon dioxide (SiO<sub>2</sub>) + Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) + Iron oxide (Fe<sub>2</sub>O<sub>3</sub>) represents at least 70% of its constitution [13], with SiO<sub>2</sub> being the most desired compound in the composition of OHA. It is well known that high amorphous SiO<sub>2</sub> availability and low carbon content are beneficial for cementitious matrices because carbon inhibits cement hydration and wraps SiO<sub>2</sub> particles, decreasing pozzolanic activity [23].

The LOI of ashes produced at different temperatures (Fig. 5) reveals that there was a significant decrease in carbon percentage and a rise in ash content between 500 and 600 °C, classifying the ashes formed at 600 °C and 700 °C as satisfying the Standard requirement.

In prior research investigating RHA, it was shown that during the combustion process, the cellulose-lignin matrix burns and leaves just a porous silica skeleton, which is the desired ash component [6]. Considering oats husks, according to the chemical composition shown in Table 2 from the EDX analysis performed on the surface of husks, the sections chosen for raw material examination did not shows a substantial quantity of silicon, which might indicate that silicon is not contained in the material's surface parts. In the ashes was not identified carbon (C), and after oxygen, the main elements found were silicon, showing off 23% average of the ashes constitution, and Potassium representing 15% average. Considering the ASTM C618 oxides requirements, the material is below the specification, representing the maximum 23.32% of the participating elements (S, Al, and Fe) for the formation of the considered oxides.

As observed with RHA, in which the increase in temperature accelerates the oxidation of organic matter [8], the OHA samples showed a reduction in carbon content and an increase in ash content, but it is not possible to relate it to the concentration of Si observed, since the ashes produced under 500° and 700 °C present concentrations higher than 600 °C, similar as observed in studies on the effect of temperature on the production of RHA [8] retained for 12 h. The dark color observed after the calcination process is known as carbon content indicative, as observed in the study of bamboo leaves ash, RHA, olive waste ash and wheat straw ash



**Fig. 3.** (a) raw material; (b) 400 °C; (c) 500 °C; (d) 600 °C; (e) 700 °C.

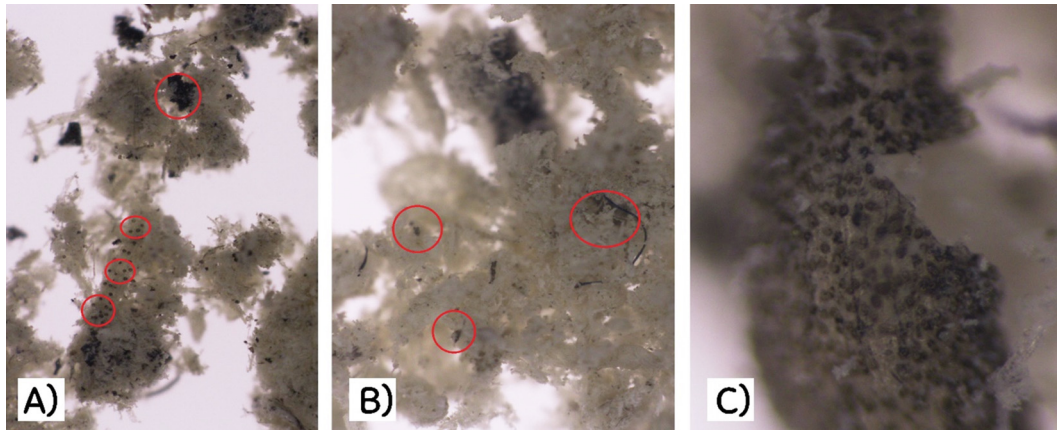


Fig. 4. (a) 500 °C magnified 5x; (b) 600 °C magnified 5x; (c) 700 °C magnified 20x.

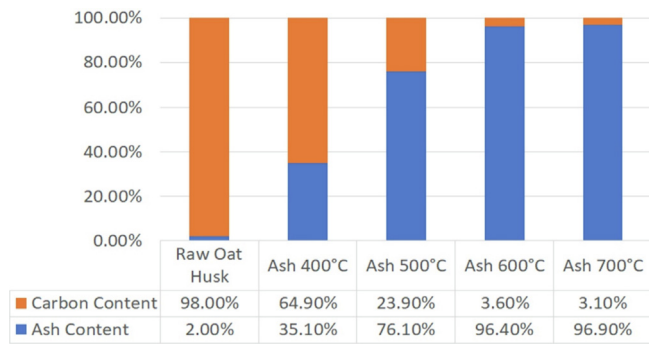


Fig. 5. Carbon and ash content of raw material and ash samples.

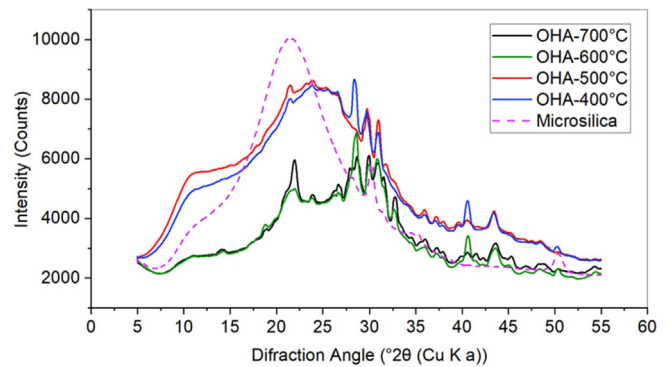


Fig. 6. Ashes and microsilica x-ray diffraction patterns.

[9] this condition for OHA was validated by the LOI results; however, the chemical composition analysis was unable to identify carbon in the ground ashes surface areas analysed. The high Potassium (K) content in the ashes may support the theory of  $K_2O$  fusion and carbon confinement. The pre-treatment of the material can be used to remove unwanted potassium and other elements, as proposed by Bandara et al, who tested the material pre-treatment using hot water to remove the metals [24] since it is known that the presence of Potassium can severely influence cement hydration, mechanical capacity, and durability [9].

### 3.4. Effects of burning temperature on the structural state of elements

Due to their atoms' greater mobility and surface position, amorphous structures are more reactive than crystalline structures; Consequently, pozzolans that demonstrate significant amounts of crystalline minerals are considered weak [25]. When compared to microsilica, the structure's crystallinity can be identified by looking at the intensity of the narrow reflections compared to the wideband around  $22^\circ (2^\circ)$  [8].

Table 2  
EDX Results of raw husks and ashes.

Component	C	O	Al	Si	Fe	K	P	S	Cl	Na	Ca	Mg	Mn
Raw (%)	35.21	59.65	0.59	3.47	0.00	0.97	0.00	0.00	0.00	0.00	0.11	0.00	0.00
400 °C (%)	0.00	51.79	0.00	24.59	0.03	13.65	2.11	1.13	1.22	0.42	3.59	1.45	0.01
500 °C (%)	0.00	49.44	0.00	22.36	0.21	16.15	2.51	1.64	1.33	0.46	4.36	1.54	0.00
600 °C (%)	0.00	45.97	0.00	21.20	0.42	16.91	4.45	1.57	1.15	0.47	5.55	2.04	0.26
700 °C (%)	0.00	46.94	0.64	23.84	0.00	15.17	2.98	1.65	1.49	0.48	4.79	2.02	0.00

The XRD patterns of the calcination products demonstrated in Fig. 6 reveal that ashes generated up to 500 °C exhibit fewer peaks, closer to the amorphous microsilica used as a reference than the others samples patterns. Between 600 and 700 °C the analyses demonstrate a non-standard abrupt shift in samples patterns, representing a rise in crystalline structures, identified by sharp non-standard peaks. In plants, the degree of present silica crystallinity is subject to burning conditions such as temperature and retention time [6]. As a result, the disparity between the samples patterns demonstrates that the OHA crystallinity is strongly associated with the production temperature, considering they were produced using the same retention time.

### 3.5. Relative density

Considering the results obtained in the LOI analysis and evaluation of the chemical composition through EDX, the ash produced at 600 °C was selected for evaluation for density and pozzolanic activity through the blend of a model mixture and its subsequent evaluation through TGA and water-bound analysis. The relative

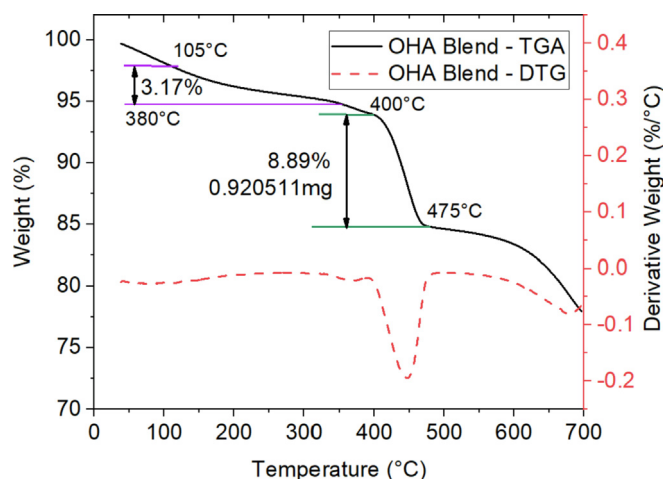


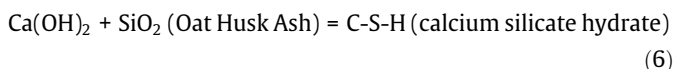
Fig. 7. TGA and DTG patterns of ashes produced at 600 °C.

density results of ashes produced under 600 °C after the grinding and reduction process for sizes less than 45  $\mu$ m were 2.78 g/ml and a standard deviation of 0.17. The results of similar study using OHA indicate that this value is 21% higher than the ash obtained at the same temperature in a similar study, which indicates an average of 2.17 g/ml [26].

Given that the calcination process removes the carbon incorporated in the OHA, promoting the opening of pores in the particle, which has already been linked to an increase in moisture absorption in RHA grains [23], the increase in density when correlated with the surface area may be an indication of the amount of organic matter present in the grains, but more research is needed.

### 3.6. Pozzolanicity

The model paste thermogravimetry analysis after 14 days of curing, as a way of evaluating the formation of reaction products of  $\text{Ca}^{++}$  and  $\text{OH}^-$  ions in the mixture, and the amorphous silica present in the ash through the reaction expressed in Equation (6), revealed the presence of peaks at around 450 °C, which may indicate the dehydroxylation of calcium hydroxide and enabling the calculation of  $\text{Ca}(\text{OH})_2$  consumption to form the product C-S-H.



The graphed results in Fig. 7 reveal a mass decrease of roughly 3.17% t between temperatures of 105 and 350 °C, which is lower than the results of oven evaluation of bound water, which showed a reduction of 4% mean and standard deviation of 0.93 for the same temperature range. The results demonstrate that 2.78 g of  $\text{Ca}(\text{OH})_2$  is consumed for the synthesis of C-H-S, indicating that the material examined has limited pozzolanic activity. Because the XRD patterns indicate the formation of peaks representing a rise in crystallinity, poor reactivity may be related to the availability of silica for the reaction, as found in RHA as a function of incineration time and temperature [8].

## 4. Conclusion

The results indicate that the increase in temperature is a factor responsible for the reduction of organic matter, evidenced by the LOI and change in the tonality of the calcined material. Despite the observed dark spots, the EDX analysis did not identify carbon in the ash composition but identified the presence of  $\text{K}_2\text{O}$ , which may be responsible for carbon confinement, so pretreatment with

hot water to remove unwanted compounds is suggested as a way to check this condition. The material studied has only 23.32% of the elements necessary for the formation of the 70% of oxides required by ASTM C618. The use of techniques such as X-Ray fluorescence microscopy or total and soluble silica can verify the formation of these oxides more accurately. The change in crystallinity in the range between 500 and 600 °C in the XRD analysis points to the opportunity to investigate this range to obtain ashes with a balance between carbon content and amorphous material.

Local oat husks in Ireland calcined between 600 °C are able to react minimally with calcium hydroxide to form calcium silicate hydrate; however, different temperatures and even more tests, such as suspension in a saturated lime solution, electrical conductivity, or standardized tests such as Chapelle test, modified Chapelle test, Fratinni method, and mechanical tests are necessary to determine the degree of pozzolanicity of this material and its behavior in cementitious mixtures.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- [1] CEMBUREAU: The European Cement Association. Activity Report. 2020.
- [2] IEA, Technology Roadmap - Low-Carbon Transition in the Cement Industry, International Energy Agency, Paris, 2018.
- [3] Council WB. World Business Council for Sustainable Development. The Cement Sustainability Initiative, Cement Industry Energy and CO2 Performance: Getting the Numbers Right, 2016.
- [4] M.C.G. Juenger, R. Snellings, S.A. Bernal, Supplementary cementitious materials: New sources, characterization, and performance insights, *Cem. Concr. Res.* 122 (2019) 257–273, <https://doi.org/10.1016/j.cemconres.2019.05.008>.
- [5] K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry, *Cem. Concr. Res.* 114 (2018) 2–26, <https://doi.org/10.1016/j.cemconres.2018.03.015>.
- [6] E. Aprianti, P. Shafiqh, S. Bahri, J.N. Farahani, Supplementary cementitious materials origin from agricultural wastes – A review, *Constr. Build. Mater.* 74 (2015) 176–187, <https://doi.org/10.1016/j.conbuildmat.2014.10.010>.
- [7] L.H.P. Jones, A.A. Milne, S.M. Wadham, Studies of silica in the oat plant, *Plant Soil* 18 (3) (1963) 358–371.
- [8] D.G. Nair, A. Fraaij, A.A.K. Klaassen, A.P.M. Kentgens, A structural investigation relating to the pozzolanic activity of rice husk ashes, *Cem. Concr. Res.* 38 (6) (2008) 861–869, <https://doi.org/10.1016/j.cemconres.2007.10.004>.
- [9] B.S. Thomas, J. Yang, K.H. Mo, J.A. Abdalla, R.A. Hawileh, E. Ariyachandra, Biomass ashes from agricultural wastes as supplementary cementitious materials or aggregate replacement in cement/geopolymer concrete: A comprehensive review, *Journal of Building, Engineering* 40 (2021) 102332, <https://doi.org/10.1016/j.job.2021.102332>.
- [10] H. Currie, C. Perry, Silica in plants: biological, biochemical and chemical studies, *Ann. Bot.* 100 (2008) 1383–1389, <https://doi.org/10.1093/aob/mcm247>.
- [11] F. Yang, J.C. Meerman, A.P.C. Faaij, Carbon capture and biomass in industry: A techno-economic analysis and comparison of negative emission options, *Renew. Sustain. Energy Rev.* 144 (2021) 111028, <https://doi.org/10.1016/j.rser.2021.111028>.
- [12] E. Schmitz, E. Nordberg Karlsson, P. Adlercreutz, R. Leegood, Warming weather changes the chemical composition of oat hulls, *Plant Biol. J.* 22 (6) (2020) 1086–1091, <https://doi.org/10.1111/plb.13171>.

- [13] ASTM C618-05. Specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM International, West Conshohocken, PA, 2010, p. 3. <https://doi.org/10.1520/C0618-05>.
- [14] F. Avet, R. Snellings, A. Alujas Diaz, M. Ben Haha, K. Scrivener, Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, *Cem. Concr. Res.* 85 (2016) 1–11, <https://doi.org/10.1016/j.cemconres.2016.02.015>.
- [15] Walter E. Dean Jr., Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods, *SEPM JSR* 44 (1974), <https://doi.org/10.1306/74D729D2-2B21-11D7-8648000102C1865D>.
- [16] O. Heiri, A.F. Lotter, G. Lemcke, Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, *J. Paleolimnol.* 25 (2001), <https://doi.org/10.1023/A:1008119611481>.
- [17] K. Scrivener, R. Snellings, B. Lothenbach, *Thermogravimetric analysis. A Practical Guide to Microstructural Analysis of Cementitious Materials*, 1st ed., CRC Press, Boca Raton, 2016.
- [18] N. Beuntner, C. Thienel, Solubility and kinetics of calcined clay: study of interaction by pore solution, in: *2nd International Conference on the Chemistry of Construction Materials*, Munich, 2016, pp. 10–12.
- [19] P.F.P. Ferraz, R.F. Mendes, D.B. Marin, J.L. Paes, D. Cecchin, M. Barbari, Agricultural residues of lignocellulosic materials in cement composites, *Appl. Sci.* 10 (2020) 8019, <https://doi.org/10.3390/app10228019>.
- [20] J. James, M.S. Rao, Silica from rice husk through thermal decomposition, *Thermochim. Acta* 97 (1986) 329–336, [https://doi.org/10.1016/0040-6031\(86\)87035-6](https://doi.org/10.1016/0040-6031(86)87035-6).
- [21] R.V. Krishnarao, J. Subrahmanyam, T. Jagadish Kumar, Studies on the formation of black particles in rice husk silica ash, *J. Eur. Ceram. Soc.* 21 (1) (2001) 99–104, [https://doi.org/10.1016/S0955-2219\(00\)00170-9](https://doi.org/10.1016/S0955-2219(00)00170-9).
- [22] D.A. Bell, B.F. Towler, M. Fan, *Gasification Fundamentals. Coal Gasification and Its Applications*, Elsevier; 2011, pp. 35–71. <https://doi.org/10.1016/B978-0-8155-2049-8.10003-8>.
- [23] J. Wang, J. Xiao, Z. Zhang, K. Han, X. Hu, F. Jiang, Action mechanism of rice husk ash and the effect on main performances of cement-based materials: A review, *Constr. Build. Mater.* 288 (2021) 123068, <https://doi.org/10.1016/j.conbuildmat.2021.123068>.
- [24] Y.W. Bandara, P. Gamage, D.S. Gunarathne, Hot water washing of rice husk for ash removal: The effect of washing temperature, washing time and particle size, *Renewable Energy* 153 (2020) 646–652, <https://doi.org/10.1016/j.renene.2020.02.038>.
- [25] R. Walker, S. Pavia, Physical properties and reactivity of pozzolans, and their influence on the properties of lime–pozzolan pastes, *Mater Struct.* 44 (6) (2011) 1139–1150, <https://doi.org/10.1617/s11527-010-9689-2>.
- [26] E. Marchetti, J. Silfwerbrand, P. Fontana, Use of Agricultural Wastes as Supplementary Cementitious Materials. School of Architecture and the Built Environment, 2020.