Evaluation of Industrial Ashes in Cement Replacement in Mortars

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Abstract. It is well known that cement production has a high negative impact on the environment. This fact, in conjunction with the high demand for this product worldwide, has created concern over how to reduce its use. Various materials have been tested as partial or total replacements for cement, one of which is biomass ash. In this article we report the preparation of test samples of mortar using two types of biomass ash, the first of forest origin and the second agricultural; both were used to replace cement in proportions of 10%, 20% and 30%. The test samples were assayed for compression and flexion after 7, 14, 28 and 90 days. After 28 days the apparent density, open porosity, absorption, capillarity and ultrasound velocity were measured. All the results of the series were compared with a control mortar. In the compression and flexion assay, a higher resistance than the control mortar was obtained with 10% replacement of both types of ash after 90 days, however with 20% and 30% ash the results were inferior to traditional mortar. There was an increase in the absorption percentage and porosity as the percentage of cement replacement increased; this increase was smaller for ash from agricultural biomass than ash from forest biomass. The density diminished as the percentage of replacement material increased, but the change was smaller with ash from agricultural biomass; this may be attributed to a filler effect produced by its granulometric distribution.

1. Introduction

Traditional cement is the most widely used construction material in the world. Its production has a great social and economic impact worldwide, considering that the construction industry accounts for 7%-10% of the economy in developed countries and 3%-6% in developing countries [1]. It also contributes around 5% of the world's CO₂ emissions into the environment, principally due to the use of fossil fuels to obtain the high temperatures required for production [2]. These high indices are a cause for concern, as the cement industry continues to grow without introducing changes to make production more environmentally friendly.

Various investigations have been carried out to evaluate the use of waste products which might replace a certain percentage of the cement used in concrete production without loss of its properties [3, 4]. Biomass ash could be a good alternative for reducing the amount of cement needed in concrete mixtures and mortars and would be a way of recycling what is generally a waste product.
Studies on the use of biomass ash to replace cement have shown that the pozzolanic reaction between biomass ash and portland cement at ambient temperature is slow, meaning that longer curing periods would be required to observe positive effects [5], but also that replacing 18% of the cement could result in a 17% reduction in CO₂ emissions [6]. Demis et. al. [7] indicate that there is an optimum replacement percentage above which the compression resistance falls. This is supported by Barbosa et. al. [8], who found that the highest compression resistance was obtained with 18% replacement, and that above 30% the resistance values were very inferior to those of the reference mixture. Lower compression resistance is influenced by various factors, such as the amount of organic material present which is related with higher water absorption and high susceptibility to abrasion [9]. The mineral composition and particle size also influence the properties of the mortar, which are affected by the characteristics of the biomass used as well as the combustion technology and the location from which the ashes are collected [7].

2. Materials and Methods

2.1. Materials

2.1.1. Portland Cement

Table 1 presents the chemical analysis of the ashes and the pozzolanic cement used in this study, which was a type P cement from ASTM.

| Composition | Cement (%) | BA1 (%) | BA2 (%) |
|-------------|------------|---------|---------|
| SiO₂        | 38.06      | 46.91   | 48.52   |
| Al₂O₃       | 8.88       | 5.85    | 5.59    |
| CaO         | 40.92      | 10.82   | 11.164  |
| Fe₂O₃       | 2.83       | 7.5     | 7.83    |
| SO₃         | 2.33       | 2.56    | 2.59    |
| MgO         | 1.59       | 2.93    | 2.63    |
| Na₂O        | 1.75       | 1.03    | 0.91    |
| K₂O         | 1.62       | 13.32   | 12.854  |
| P₂O₅        | -          | 3.43    | 3.17    |
| Cl          | -          | 3.54    | 2.49    |
| TiO₂        | -          | 0.874   | 0.84    |
| Cr₂O₃       | -          | 0.171   | 0.194   |
| MnO         | -          | 0.5     | 0.5     |

Table 1. Chemical properties of the cement and the biomass.

2.1.2. Biomass ash

Both the biomass produced from wood and forest waste (BA1) and the biomass produced from agricultural waste (BA2) were collected in the forests of the Araucanía Region of Chile, where the biomass combustion plants are located. Biomass combustion produces two types of materials: fly ash and bottom ash. In this case bottom ash was used.
2.2. Mixture proportion

The mixture proportions of the mortars are shown in Table 2. To analyse the influence of the two types of waste, 7 mortar mixtures were prepared. They were calculated with a cement-sand ratio of 1:3 and water-cement ratio of 0.55.
The cement replacements were added in proportions of 10%, 20% and 30% weight for both types of biomass ash.

|   | Water (g) | Cement (g) | BA1 (g) | BA2 (g) | Sand (g) | Consistency (mm) |
|---|-----------|------------|---------|---------|----------|------------------|
| BC | 270       | 450        | 1350    |         | 163.3    |
| BA1-10 | 270   | 405        | 45      | 1350    | 165.2    |
| BA1-20 | 270   | 360        | 90      | 1350    | 156.5    |
| BA1-30 | 270   | 315        | 135     | 1350    | 148.6    |
| BA2-10 | 270   | 405        | 45      | 1350    | 170.3    |
| BA2-20 | 270   | 360        | 90      | 1350    | 166.2    |
| BA2-30 | 270   | 315        | 135     | 1350    | 161.9    |

2.3. Assay methods

2.3.1. Consistency
The fluidity of the mortar was determined as established in Standard UNE-EN1015-3 of the Spanish Association of Normalization and Certification. A mini-slump flow cone with 100 mm internal diameter was used on a 250mm flow table disc. The following steps were followed: The mould was filled with fresh mortar and then lifted vertically to spread the mortar on the disc, shaking the flow table at constant frequency 15 times. Finally, two perpendicular extension diameters of the mortar were measured and recorded.

2.3.2. Dry density
The dry density ($\rho_d$) was obtained as indicated in Standard UNE-EN 1015-10, using 3 cylindrical test samples of 100 mm diameter and 50 mm height. These measurements were taken after 28 days and 90 days of curing. First the samples were dried for a minimum of 24 hours in an oven at 105ºC and the dry weight was measured (A). Then they were submerged in water for 24 h and the saturated weight was measured (B). Finally the weight of the sample in suspension in water was taken to obtain the submerged weight (C). The dry density was calculated using the formula given by equation (1)

$$\rho_d = \left[ \frac{A}{B - C} \right] \cdot \gamma$$

where $\gamma$ is the water density equivalent to 1 g/cm$^3$.

2.3.3. Water-accessible porosity
The water-accessible porosity ($P_a$) is calculated from the dry density information, following the ratio established in equation (2), as per Standard UNE-EN 1015-18

$$P_a = \frac{B - A}{B - C} \cdot 100$$


2.3.4. Water absorption by immersion
The water absorption by immersion, Abs (%), is calculated according to Standard UNE-EN 1015-18 from the dry density data, applying the formula given by equation (3)

$$\text{Abs} (%) = \frac{B - A}{A} \cdot 100$$  \hspace{1cm} (3)

2.3.5. Capillary absorption test
The water absorption rate was determined according to ASTM Norm C1585, using three cylindrical test samples of 100mm diameter and 50 mm height, in which the mass increase was controlled for the absorption of water over time.

The slope of the graph of absorption-square root of time, for periods between 1 min and 6 hours, was used to obtain the initial water absorption rate (cm / s^{1/2}). The capillary absorption coefficient (K) was obtained with equation (4)

$$K = \frac{Q}{A \cdot \sqrt{t}}$$  \hspace{1cm} (4)

where K is the coefficient of capillarity (cm / s^{1/2}); Q is the quantity of water absorbed (cm³); A is the area of the surface exposed to water (cm²) and t is the time (s).

2.3.6. Mechanical properties (compression and flexion)
To obtain the resistances to compression and flexion, three different prismatic samples, dimensions 4 cm × 4 cm × 16 cm, were tested for each series after 7, 14, 28 and 90 days of curing, following Norm UNE-EN 196-1.

2.3.7. Ultrasound Pulse Velocity
The ultrasound pulse velocity method is used to check both the homogeneity of the mortar and the presence of cracks or bubbles, possible variations in properties over time, and to determine the physical and dynamic characteristics of the material. The ultrasound pulse velocity (UPV) test determines the propagation velocity of a sound wave in a given material, detecting the time the wave takes to cross a certain thickness. For this method, the assays are carried out on 3 cylindrical test samples of 100mm diameter and 50mm height following ASTM Norm C597-02, using a UPV Controls test instrument. The time the ultrasound pulse takes to travel through the sample is measured to an accuracy of 0.1 μs, using 54 kHz transducers placed in the centre of the opposing face of each cylindrical sample.

3. Results and discussion.

3.1. Dry density, water absorption and open porosity
With 10% of the cement replaced by biomass, an increase was observed in the density with both BA1 and BA2 (Fig. 3); however, when the replacement percentage was increased, a linear reduction was found in each series. This reduction was greater in series BA1, where 30% replacement produced a fall of 5.49% in the density as compared with the control mixture; the reduction was gentler in BA2, where a 30% replacement produced a diminution of 1.36% in the density as compared with the control. This result is probably due to the lower density of the ashes used as compared to the density of cement. Carrasco et. al. [10], obtained a similar result in their experiment where they carried out density tests on blocks with replacement of 10% to 90% of cement by biomass ash, obtaining a progressive diminution as the replacement percentage increased.
The absorption (Fig. 4) shows an increase in the series of each biomass as the replacement percentage increased; the increase is greater for BA1, reaching 14.75% absorption with 30% replacement. BA2 presents a more gradual rise reaching 13.73% absorption with 30% replacement. Rajamama et. al. [11] note that these increases are related with the particle size used, which is smaller in BA1 than in BA2. The use of wastes with smaller granulometry results in a greater filler effect; this means that more pores are filled, resulting in more compact and therefore fewer absorbent matrices. Chowdhury et. al. [12] obtained a similar increase using forest waste.
The porosity (Fig. 5) presents an increase with the incorporation of biomass. The values for BA1 are lower than those for BA2 with 10% and 20% replacement, however with 30% replacement the porosity obtained was 27.3% for BA1 and 26.51% for BA2. The increase in porosity is related with the reduction in density, and the larger particle size of BA2 compared with BA1 correlates with the higher porosity values in BA2.

Figure 4. Absorption percentage of mortar samples

Figure 5. Percentage of pores in mortar samples
3.2. Water absorption by capillarity

The capillarity (Fig. 6) increases as the replacement percentage increases. The change is more abrupt for the BA2 series, where a value of 1.886*10^-4 cm/s^{0.5} is reached with 30% replacement, compared to 1.261*10^-4 cm/s^{0.5} for the BA1 series. BA2 presents higher values due to its larger particle size and pore percentage.

![Capillarity results for mortar samples](image)

3.3. Resistance to compression and flexion

BA1 samples at 10% replacement present lower compression resistance values after 7, 14 and 28 days (Fig. 7); however, at 90 days the value is 33.93 MPa, an increase of 1.92% over the control. Something similar occurs for BA2 at 10% replacement: at 28 days it already presents a similar resistance to the control, and at 90 days it reaches a value of 34.67 MPa, an increase of 4.14% over the control. This agrees with Targan et al. [3], who reported that mixtures with biomass ash require a longer curing time to reach maximum resistance.

As the replacement percentage increases, the compression resistance values are seen to fall; this is consistent with the greater porosity and water absorption, and the lower pozzolanicity of the ash compared to portland cement.
The test samples at 10% biomass replacement presented higher flexion resistance values after 28 days than the control (Fig. 8). The increase recorded was 8.4% for BA1 and 17.97% for BA2, however after 90 days the values were lower than the control by 8.3% for BA1 and 2.59% for BA2.

For the series with 20% and 30% replacement, all the results were inferior to the control sample, by over 20% in both biomass types after 90 days. Martínez-Lage et. al. [13] obtained similar values for flexion resistance with 10% replacement, however for 20% and 30% replacement they obtained smaller diminutions than in the present study, probably due to the degree of pozzolanity of the ashes analysed.
3.4. Ultrasound Pulse Velocity
The velocity obtained for the control sample was 4232 m/s. This was exceeded only by BA2 with a velocity of 4247 m/s for the mixture with 10% replacement. All the other samples presented lower values than the control; however, they were in a range between 3500 m/s and 4000 m/s, which is considered good in the pertinent regulations.

![Figure 9. Results of ultrasound pulse velocities](image)

4. Conclusions
The results obtained with 10% replacement of cement by biomass ash show very similar behaviour to the control sample, with both BA1 and BA2. Their compression resistance increases without severe alterations in their other properties; however, the replacement percentages of 20% and 30% proved to be unsuitable for use.

The granulometry of the ashes is directly related with the properties of the mortar mixtures. In most of the results, BA1 presented less variation than BA2, which had a larger particle size. Finer particles result in a more compact matrix, with less absorption, meaning that less water will be needed for making up mortars.

The use of 10% biomass ash to replace cement also implies the use of a smaller amount of cement and allows the biomass ash to be recycled.

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References
[1] Lowe, J. L. (2003). Construction Economics. Obtained from www.callnetuk.com/home/johnlowe70
[2] Worrel, E., Price, L., Martin, N., Hendriks, C., Ozawa, L. (2001). Carbon Dioxide Emissions From The Global Cement Industry. *Annu. Rev. Energy Environ.*, 26:303-29.
[3] Letelier, V., Ortega, J.M., Muñoz, P., Tarela, E., Moriconi, G. (2018). Influence of Waste brick powder in the mechanical properties of recycled aggregate concrete. *Sustainability*
10(4), 103. doi: 10.3390/su10041037.

[4] Letelier, V., Tarela, E., Muñoz, P., Moriconi, G. Assessment of the mechanical properties of a concrete made by reusing both: Brewery spent diatomite and recycled aggregates. Construction and Building Materials 114, pp. 492-498. doi: 10.1016/j.conbuildmat.2016.03.177

[5] Targan, S., Olgun, A., Erdogan, Y., Sevinc, V. (2003). Influence of natural pozzolan, colemanite ore waste, bottom ash, and fly ash on the properties of Portland cement. Cement and Concrete Research 33, 1175-1182. doi:10.1016/S0008-8846(03)00025-5

[6] Ecosmart Concrete. (2008). Environmental impact – cement production and the CO2 challenge. Canada: Ecosmart Foundation.

[7] Demis, S., Tapali, J. G., Papadakis, V. G. (2014). An investigation of the effectiveness of the utilization of biomass ashes as pozzolanic materials. Construction and Building Materials 68, 291-300. doi:http://dx.doi.org/10.1016/j.conbuildmat.2014.06.071

[8] Barbosa, R., Lapa, N., Dias, D., Mendes, B. (2013). Concretes containing biomass ashes: Mechanical, chemical, and ecotoxic performances. Contraction and Building Materials 48, 457-463. doi:http://dx.doi.org/10.1016/j.conbuildmat.2013.07.031

[9] Beltrán, M. G., Barbudo, A., Agrela, F., Jiménez, J. R., De Brito, J. (2016). Mechanical performance of bedding mortars made with olive biomass bottom ash. Contraction and Building Materials 112, 699-707. doi:http://dx.doi.org/10.1016/j.conbuildmat.2016.02.065

[10] Carrasco, B., Cruz, N., Terrados, J., Corpas, F. A., Pérez, L. (2014). An evaluation of bottom ash from plant biomass as a replacement for cement in building blocks. Fuel 118, 272-280. doi:http://dx.doi.org/10.1016/j.fuel.2013.10.077

[11] Rajamma, R., Senff, L., Ribeiro, M. J., Labrincha, J. A., Ball, R. J., Allen, G. C., Ferreira, V. M. (2015). Biomass fly ash effect on fresh and hardened state properties of cement based materials. Composites Part B 77, 1-9. doi:http://dx.doi.org/10.1016/j.compositesb.2015.03.019

[12] Chowdhury, S., Mishra, M., Suganya, O. (2015). The incorporation of wood waste ash as a partial cement replacement material for making structural grade concrete: An overview. Ain Shams Engineering Journal, 429-437. doi:http://dx.doi.org/10.1016/j.asej.2014.11.005

[13] Martinez-Lage, I., Velay-Lizancos, M., Vázquez-Burgo, P., Rivas-Fernández, M., Vázquez-Herrero, C., Ramírez-Rodríguez, A., Martin-Cano, M. (2016). Concretes and mortars with waste paper industry: Biomass ash and dregs. Journal of Environmental Management 181, 863-873. doi:http://dx.doi.org/10.1016/j.jenvman.2016.06.052