sustainability

MDPI

*Article*

# Properties of Precast Concrete Using Food Industry-Filtered Recycled Diatoms

**Carlos Rodriguez [1,*], Isabel Miñano [2], Carlos Parra [2], Pedro Pujante [3] and Francisco Benito [2]**

[1] Department of Construction Materials, Centro Tecnológico de la Construcción, 30820 Alcantarilla, Spain
[2] Department of Architecture and Building Technologies, Technical/Polytechnic University of Cartagena, 30203 Cartagena, Spain; isabelminano@hotmail.com (I.M.); Carlos.Parra@upct.es (C.P.); franciscojavierbenito@hotmail.es (F.B.)
[3] Technical Department, Bortubo S.A., 30620 Murcia, Spain; crodriguez@ctcon-rm.com
* Correspondence: carloslrl@hotmail.com; Tel.: +34-605-817-455

**Abstract:** The concrete industry is under increasing pressure to reduce greenhouse gas emissions. An immediate solution is to minimize the amount of Portland cement used by partially substituting other supplementary cementitious materials. This article presents the results of an experimental campaign on the influence of replacing Portland cement with both calcined and uncalcined diatomites from the filtration of beer and wine in the production of elements made of vibro-pressed pre-cast concrete, such as pipes. Additionally, a natural diatomite is used. The mechanical properties, capillary water absorption, carbonation, and chloride ingress are tested. The results obtained show the possibility of using natural and recycled diatomites on an industrial scale, which can improve even the long term properties of prepared precast concrete.

**Keywords:** compressive strength; durability; diatomite; recycled diatomites; concrete; precast concrete

check for updates

**Citation:** Rodriguez, C.; Miñano, I.; Parra, C.; Pujante, P.; Benito, F. Properties of Precast Concrete Using Food Industry-Filtered Recycled Diatoms. *Sustainability* **2021**, *13*, 3137. https://doi.org/10.3390/su13063137

Academic Editor: Jorge de Brito

Received: 17 February 2021
Accepted: 7 March 2021
Published: 12 March 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

One of the primary challenges for the cement industry in the coming decades will be to reduce greenhouse gas emissions, particularly carbon dioxide. It is estimated that this manufacturing process generates approximately 0.87 tonnes of $CO_2$ for every ton of Portland cement [1].

Additionally, this process requires a high consumption of natural resources and thermal energy (3600 MJ/tonne of clinker), the latter due to the high temperatures (1400–1500 °C) required in the production of the clinker [2]. A document published in late 2009 called Cement Technology Road Map by the International Energy Agency (IEA) and World Business Council for Sustainable Development (WBCSD) [3], shows the proposed solutions to achieving environmental sustainability in the sector, such as: increased energy efficiency; use of alternative fuels; partial replacement of the clinker with supplementary materials and/or additions; search for new raw materials, among others. Replacement of the clinker substitution is showing immediate results, effectively enabling some companies to already reduce $CO_2$ emissions by 25–30% [4].

Blended cements correspond to cements with a partial substitution of clinker for inert mineral additions (limestones) or chemically active additions, such as pozzolanas (silica smoke, metakaolin, fly ash, rice shell ash) or blast furnace steel slag [5]. These cements may or may not present, depending on the type, a quality and quantity of additional technical advantages such as a lower water demand, reduced hydration heat, reduced porosity, and good behavior against aggressive media [6–8]. However, the strategy of replacing clinker with supplementary cementitious materials is currently at risk, we could potentially run out of the most widely used sources of supplementary cementitious materials, such as fly ash and ground granulated blast furnace slag. This problem is driving research to find alternative sources of these materials.

Diatomaceous earth, diatomite or kieselguhr, is a naturally occurring, soft, siliceous sedimentary rock that is composed of the silica skeleton of diatoms. World production in 2013 was 2.3 Mt [9], of which 61% is used as a filter [10]. Given the microporous structure of fossilized diatoms, they are a good filter of microscopic particles. During the manufacture of beer, wine, and oil, among others, it is used in the purification phase of the product to give it clarity by retaining organic particles that, in the previous processes, have not been retained. Once the porous network of the diatomite is filled, they become useless for filtering owing to the high cost of cleaning.

Diatomite is characterized as a natural pozzolan [11,12], satisfying the requirements concerning the active silica content of EN 197-1 [5]. It has been proven that replacing a percentage of Portland cement with natural diatomite can significantly improve the properties of concrete [13], allowing for the reduction of both the cost of the concrete and the $CO_2$ emissions that are made during the production of cement. However, diatomites are not frequently used in the construction industry in Spain. The pozzolanic reaction of diatomite leads to the formation of higher amounts of hydrated products, especially at the age of 28 days. The pozzolanic activity, porosity, and grindability of diatoms can be improved by calcination [14,15]. During the work, raw diatomite-blended cements were obtained by replacing the clinker with raw diatomite at various rates to manufactured mortars. Comparable strength was achieved by un-calcined diatomite with an up to 10% clinker replacement level, while comparable strength was achieved by calcined diatomite up to 20%, as a result of the study. Conversely, a higher water demand also was observed as the percentage of diatomite used increased, which resulted in a decrease in strength. The same has been observed in other studies [12,14,16–18]. Furthermore, another study carried out in a laboratory used block elements with diatomite as a substitute for aggregates and researched the effect of these parameters on the physical and mechanical properties of concrete blocks, producing good results [19]. During this study, the slump of fresh concrete was zero, typical for this type of product. Other studies with precast concrete elements in industry [20], showed that the use of raw materials with high water absorption can be used in this application with the same quantity of effective water used in the original dosages from companies. No work with diatomite in industrial precast concrete has been found in the bibliographical literature.

Capillary water absorption in concrete is of major significance for the durability assessment of concrete structures. Water absorption of the specimens containing diatomite powder was lower than that of the control specimen [18]. During this study, the maximum reduction in water absorption was observed in samples containing 30% of diatomite powder. Furthermore, experimental results indicated that the sulfate resistance of mortars made with diatomite was better than that of the control mortar [13]. The same was observed in another study [21], where the acid and sulfate resistance properties of mortars were improved by the presence of minerals. When studies in the literature are examined, it is understood that the influence of diatomite on the durability properties of mortars and concretes still needs to be evaluated.

Only one work with recycled diatomite has been found in the bibliographical literature [22], where the diatomite was obtained from a brewery. Diatomites are a serious environmental and economic problem as they are by products that, after an industrial process, cannot be used. The volumes generated are large, and the cost of their deletion is disproportionate. Being able to grant them another use, or use in any productive activity, is a highly desirable objective, directly for waste generators and indirectly for potential users of the waste as a lower cost alternative raw material than the conventional. Therefore, and due to the large volume of national production in Spain, large quantities of diatomaceous earth are generated, filled, and made useless, without another useful life. Accompanying the use of recycled diatomite, a dual environmental benefit occurs, on the one hand, the replacement of part of the cement and, on the other hand, the disposal of industrial waste which would not need to be deposited in controlled landfills. Therefore, the novelty of this research is to analyze the effects on the mechanical properties and the durability of the

replacement by recycled calcined and uncalcined diatomites from the filtration of beer and wine as cement in the production of elements made of vibro-pressed pre-cast concrete such as pipes. Particularly, the water demand, mechanical properties (compressive strength, strength), and durability (water absorption, chloride ingress, carbonation) of pipes are tested.

## 2. Materials and Methods

### *2.1. Materials*

The cement type used was a CEM I 42.5R according to the Spanish standard UNE-EN 197-1 [5]. Its chemical composition is summarized in Table 1. The Blaine fineness of the cement was 3420 $cm^2/g$.

**Table 1.** Chemical composition of cement and diatomites (%), major compounds, and amorphous material (%). Tested by X-Ray fluorescence, thermogravimetric analysis, and X-ray diffraction.

| Oxides | Cement Type I | Natural Diatomite | Recycled/Wine | Recycled/Beer |
|---|---|---|---|---|
| $Na_2O$ | 0.37 | 0.20 | 2.07 | 0.71 |
| MgO | 2.52 | 0.68 | 0.15 | 0.54 |
| $Al_2O_3$ | 4.09 | 1.77 | 2.37 | 3.91 |
| $SiO_2$ | 16.89 | 54.82 | 90.67 | 82.36 |
| $K_2O$ | 1.33 | 0.33 | 0.19 | 0.92 |
| CaO | 64.74 | 19.98 | 0.80 | 0.44 |
| $TiO_2$ | 0.26 | 0.09 | 0.50 | 0.29 |
| $Fe_2O_3$ | 3.51 | 0.78 | 2.14 | 2.84 |
| $P_2O_5$ | 0.18 | 0.14 | 0.09 | 0.22 |
| $SO_3$ | 4.06 | 0.22 | 0.03 | 0.30 |
| LOI | 0.92 | 20.65 | 0.85 | 7.27 |
| LOI before the filtration process | - | - | 0.81 | 4.35 |
| Amorphous | - | 67.9 | 65.4 | 69.6 |
| Amorphous after heat treatment | - | - | 81.6 | 82.5 |

Crushed limestone was used as the aggregate. Aggregates with a density of 2.72 $g/cm^3$ and a water absorption of 1% in the fine fraction and 0.50% in the coarse fraction, with a maximum grain size of 12 mm were used. The granular skeleton was composed of two fractions of crushed limestone aggregate: 4/12 mm coarse aggregate and 0/4 mm fine aggregate, with a fine content (particle size < 0.063) of 1.0 and 17.1%, respectively.

Diatomites from different sources were used. During this study, a natural diatomite and recycled diatomites from filtering by the food industry with and without heat treatment were used. The natural diatomite (ND) used in the research were supplied by CEKESA, whose quarries are located in Hellín (Spain). The recycled diatomites used were from the filtration of beer (BeerD) and wine (WineD), supplied respectively by Estrella Levante and Bodegas Jumilla (Spain). The pH and apparent density are shown in Table 2. The pH of diatomite sludge depends on the pH of the filtered medium. All the diatomites used had a particle size below 40 microns.

**Table 2.** Characterization of diatomites.

| Type Diatomite | pH | Apparent Density ($g/cm^3$) |
|---|---|---|
| | | UNE-EN 1097 |
| ND | 6.87 | 0.34 |
| WineD | 7.72 | 0.24 |
| BeerD | 4.89 | 0.41 |

The chemical composition realized by X-ray Fluorescence (XRF) is presented in Table 1 for different diatomite samples. Diatomites are high in silica, carbonates, and soluble impurities; therefore, their pozzolanic activity is related to their silica component in the vitreous state. To determine the volatile components, including the organic matter content, loss on ignition (LOI) at 1100 °C of the diatomites before and after the filtration process was performed. Table 1 shows the results of LOI and the percentage of active silica. Seen in the Table, the organic matter content of the BeerD was high (2.92%) and could cause setting inhibition problems. Therefore, a heat treatment was used on the recycled diatomites (900 °C for 2 h). This procedure also allowed us to increase the reactive silica [14], as can be seen in the results obtained. Recycled diatomites without heat treatment were dried for two days on the stove at 60 °C. All cementitious materials (cement, ND, BeerD, WineD) used in the study are shown in Figure 1.




**Figure 1.** Cement, ND, BeerD and WineD used in the study.

### 2.2. Concrete Mixtures and Products

Concrete pipes of a 300 mm diameter were made. The dimensions in mm are shown in Figure 2.

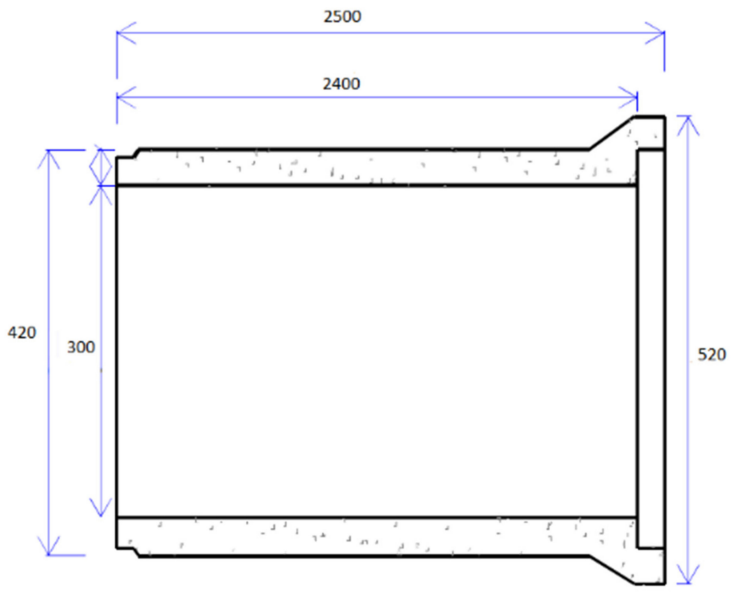



**Figure 2.** Geometrical dimensions (in mm) of pipes used in this study.

The products were manufactured with two different percentages of cement replaced by diatomites at 15 and 30%. The concrete mix design is shown in Table 3. The nomenclature used refers first to the control concrete (Control), the type of diatomite—natural (ND), wine (WineD), beer (BeerD)—the percentage of diatomites used, 5% (5) and 15% (15) and, finally, the use of recycled calcined diatomites (C).

**Table 3.** Mix proportions of different prepared concretes.

| Mixture | Cement ($kg/m^3$) | Water ($l/m^3$) | Coarse Aggregate ($kg/m^3$) | Fine Sand ($kg/m^3$) | Natural Diatomite ($kg/m^3$) | Recycled Beer Diatomite ($kg/m^3$) | Recycled Wine Diatomite ($kg/m^3$) |
|---|---|---|---|---|---|---|---|
| Control | 242 | 145.2 | 550 | 1450 | | | |
| ND-5 | 229.9 | 145.2 | 550 | 1450 | 12.1 | | |
| ND-15 | 205.7 | 145.2 | 550 | 1450 | 36.3 | | |
| WineD-5 | 229.9 | 145.2 | 550 | 1450 | | | 12.1 |
| WineD-15 | 205.7 | 145.2 | 550 | 1450 | | | 36.3 |
| WineD-5-C | 229.9 | 145.2 | 550 | 1450 | | | 12.1 |
| WineD-15-C | 205.7 | 145.2 | 550 | 1450 | | | 36.3 |
| BeerD-5-C | 229.9 | 145.2 | 550 | 1450 | | 12.1 | |
| BeerD-15-C | 205.7 | 145.2 | 550 | 1450 | | 36.3 | |

During the production, it was checked that all the mixes had the same slump cone as the reference concrete (0–1 cm). Once all the products were made, they were sent directly to the curing concrete area of the company, where they remained for 28 days before being tested. Test specimens also were made and cured in the laboratory, submerged in water.

These types of prefabricated elements were made through a radial compression process. The manufacture of the materials is shown in Figure 3.



**Figure 3.** Industrial pipe manufacturing process.

### 2.3. Methods

The slump cone test [23], mechanical properties, and durability of the concretes prepared at the company, Bortubo, were tested. Regarding each test and age, triplicate samples were used. The results presented in the following sections are the average value of the obtained results.

The compressive strength of the concrete was tested according to the standard UNE-EN 12390-3 [24] at 28 and 90 days. Regarding the concrete pipes, the strength of the samples was determined by tests at 28 days, according to the UNE EN 1916 [25], as shown in Figure 4.




**Figure 4.** Strength test according to the UNE EN 1916.

The durability of the types of concrete was tested using different methods. The capillary water absorption of the concretes at 90 days was determined following the recommendations of the standard UNE 83982 [26]. The resistance of the concrete to chloride ingress after 90 days was determined using the standard AASHTO T259 [27]. According to this standard, the samples with dimensions 100 mm × 100 mm × 400 mm were placed inside a curing chamber for 76 days, and in a drying chamber for 90 days. Side faces were protected with an impermeable material to create a watertight area where a dissolution with 3% sodium chloride was introduced. The amount of dissolution was controlled to ensure a minimum thickness of 15 mm for the dissolution layer. Occurring at the testing age, a slice was cut off the sample and sprayed with silver nitrate to determine the penetration depth of the chlorides. Even though this method does not allow for the calculation of any diffusion coefficient, it is very useful for the direct comparison of different types of concrete regarding their resistance to chloride ingress. The carbonation resistance of concrete after 90 days (accelerated method) was determined according to the standard UNE 83993-2 [28]. The samples for this test, at a given age, which were prismatic with the dimensions 100 mm × 100 mm × 400 mm, were prepared by homogenizing the moisture content. They were stored in a climate chamber under the following conditions: 3% $CO_2$, 21 ± 2 °C, and 60 ± 10% moisture content. Using a 3% $CO_2$ air concentration, the obtained hydrated cement reaction products were the same as in a regular atmosphere with a 0.03% $CO_2$ content. Occurring at 90 days, a test piece portion of approximately 50 mm was broken to determine the carbonation depth using the phenolphthalein method.

## 3. Results and Discussion

### *3.1. Slump Cone Test*

Table 4 shows all the slump cone results obtained in accordance with UNE-EN 12350-2 [23]. All the dosages made with diatomites, regardless of the percentage of substitution, have the same slump cone as the reference concrete (0–1 cm). Therefore, it is possible to obtain mixtures with the same workability required for the manufacture of this type of product without the need to use additives or increase the water content of the dosages. During other studies [12,14,16,17], it was evidenced that the use of diatomites generated a greater water demand due to the fact that the porous structure of the diatomite absorbs more water [29]. This higher water demand, through the increase in the percentage of diatomite, generally results in a decrease in strength.

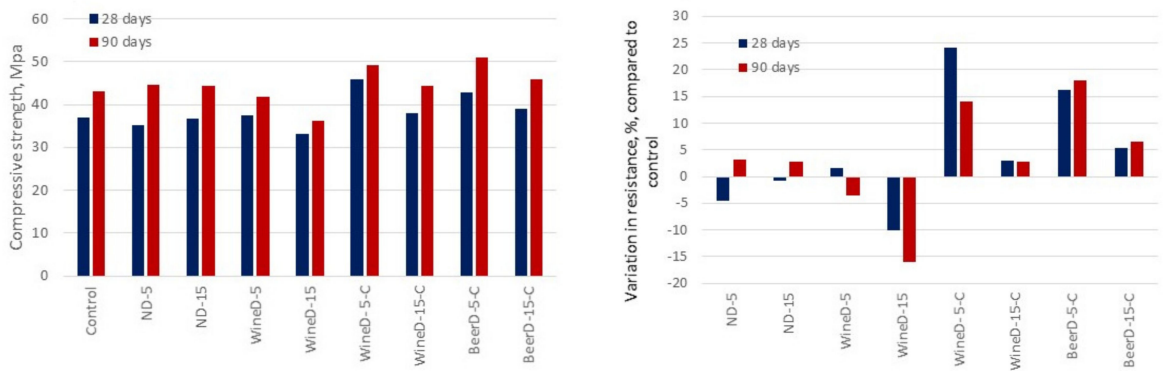
**Table 4.** Results of durability and slump tests.

| Type | Capillary Suction Coefficient K, $\times 10^{-3}$ kg/(m$^2$·s$^{0.5}$) | Carbonation Depth (mm) | Chloride Penetration Depth (mm) | Slump Cone (cm) |
|---|---|---|---|---|
| Control | 5.7 | 7.6 | 15.6 | 1 |
| ND-5 | 6.7 | 8.7 | 14.2 | 1 |
| ND-15 | 5.4 | 7.6 | 12.6 | 0 |
| WineD-5 | 5.8 | 7.8 | 17.1 | 1 |
| WineD-15 | 9.8 | 13.8 | 18.4 | 1 |
| WineD- 5-C | 5.4 | 7.7 | 13.1 | 0 |
| WineD-15-C | 5.2 | 8.1 | 12.1 | 0 |
| BeerD-5-C | 5.6 | 7.4 | 13.8 | 0 |
| BeerD-15-C | 5.0 | 8.4 | 11.4 | 0 |

Therefore, results here indicate that the use of natural and recycled diatomites as a cement substitute, up to a replacement percentage of 15%, can be used in dry consistency concrete without the need to increase the water content.

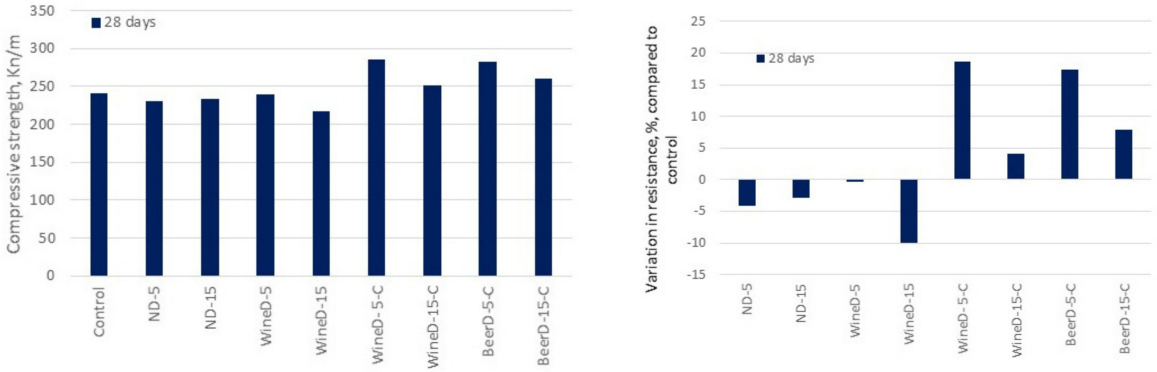
### *3.2. Compressive Strength and Mechanical Capacity of Concrete Pipes*

The compressive strength of the concretes was measured following the standard UNE-EN 12390-3 [24], at 28 and 90 days, and the strength of the concrete pipes was determined by tests at 28 days according to the UNE EN 1916 [25]. The results of the concrete and pipe strengths are shown in Figures 5 and 6.




(**a**) (**b**)

**Figure 5.** (**a**) Compressive strength of the concretes, as compared to control; (**b**) variation in resistance regarding the average value of the control concrete.




(**a**) (**b**)

**Figure 6.** (**a**) Strength of pipes, as compared to control; (**b**) variation in strength regarding the average value of control concrete.

The compressive strength of concrete with 5 and 15% natural diatomite has similar strength to the reference concrete. During other studies, improvements in strength were observed for up to 10% substitutions [11]. The degree of resistance obtained depends mainly on the reactivity of the diatomite. The main influencing factors are: (a) the percentage of reactive $SiO_2$, which will influence the pozzolanic reaction of the diatomite with portlandite; (b) the filler effect; (c) the dilution effect; (d) the fineness of the diatomite.

The use of untreated recycled diatomites (wineD) maintains the strength regarding the control concrete for up to 5% substitutions. When the percentage is increased to a 15% substitution, there is a 15% loss of strength at 90 days. Looking at the high silica content, the percentage of reactive silica, and the fineness of these diatomites compared to natural diatomite, another behavior would have been expected. The main cause explaining these results is the organic matter content of WineD (0.04%), which partially inhibits setting of the cement. Regarding the case of BeerD samples with a higher organic matter content (2.92%), it was observed in previous tests that the samples did not set, confirming this hypothesis. During another study [22], where 5%, 10%, and 15% of brewery-spent untreated diatomite were used, the obtained results were similar to those obtained in this study. The use of untreated recycled diatomite at up to a 5% substitution did not produce strength losses, and even produced improvement.

The heat treatment performed on WineD and BeerD improved the behavior obtained due to the increase of the reactive $SiO_2$. Samples with 5% calcined recycled diatomite (wineD-5-C, BeerD-5-C) increased the strength by about 15% at 90 days with respect to the reference concrete. The use of a 15% substitution slightly improved the results obtained with respect to the control sample. The use of a heat treatment, in addition to eliminating organic matter, had another positive effect by increasing the reactive $SiO_2$ content, which generated concretes with higher strength. The $SiO_2$ reacted with $Ca(OH)_2$ and produced calcium silicate hydrates (CSH), which were responsible for the increase in strength. This same effect on calcined diatomites was reported by other research [14,30]. The maximum pozzolanic activity was attained from the mortars produced with diatomite calcined at 850 °C [30].

The strength results obtained in tubes (Figure 6) were similar to those obtained in the manufactured concrete specimens, as expected. All samples studied, both natural and recycled, had a similar or higher strength than the control sample, with the exception of the WineD-15 dosage, which produced a 10% loss in strength. All concretes studied satisfy the requirements of the UNE EN 1916 standard for pipes [25]. Therefore, this application can be very suitable for this type of addition.

### *3.3. Capillary Water Absorption*

One of the main parameters related to the durability of concrete is capillary water absorption. This parameter is related to the porosity and tortuosity in concrete, as well as the velocity of the ingress of aggressive substances into concrete [31]. The capillary suction coefficient, K, is linked to the velocity of water penetration into concrete. The results for the capillary suction coefficient measured at 90 days are presented in Table 4 and Figure 7.

Seen in the concretes prepared with diatomite, there was a reduction in capillary water absorption when 15% diatomite was used to replace cement, with the exception of the WineD-15 sample, which had a higher porosity due to the organic matter content. The main reasons why the use of diatomites improves density are the filler effect and the pozzolanic reaction between the amorphous silica of the mineral addition, and the calcium hydroxide produced by the hydration reactions of the cement results in the paste being more homogeneous and denser. The same also was observed in another study [18], where water absorption of the specimens containing diatomite powder was lower than that of the control specimen. The maximum reduction of 28% in water absorption was observed in samples containing 30% diatomite powder.

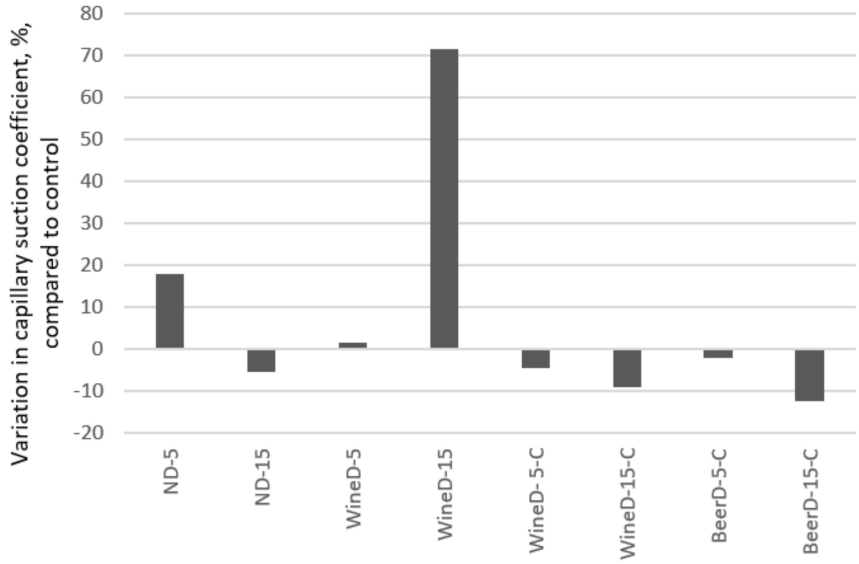



**Figure 7.** Variation in the capillary suction coefficient regarding the average value of the control concrete.

The use of 5% diatomite generates concretes with different absorption depending on the type of diatomite used. Concretes with natural diatomite and WineD-5 have a higher or similar absorption to that of the reference concrete. Conversely, when using recycled diatomites that have undergone a calcination process (WineD-5-C, BeerD-5-C), the water absorption of the concrete is reduced. These results are explained by the fact that the heat treatment increases the reactivity of the diatomites, making the concrete less porous and more durable. This hypothesis becomes more evident when the substitution rate increases to 15%. The efficiency of natural and recycled diatomites as additions is confirmed by these results, and are in agreement with the behaviour of active additions regarding the capillary suction of concrete [8].

The use of untreated recycled WineD diatomites up to a 5% substitution produces concretes with similar porosity but, when this percentage is increased, there is an important increase in the velocity of the ingress of water in concrete samples due to the organic matter content.

### *3.4. Resistance to Carbonation*

The results for the carbonation depth at 90 days, as well as its variation with respect to the control samples, are shown in Table 4 and Figure 8.

The mixtures had a similar or slightly lower behavior versus the depth of carbonation in the concretes with a percentage of 5 and 15% of natural and recycled diatomites with respect to the reference mixture, without any addition. The content of CaO and alkaline (sodium and potassium) are the materials susceptible to carbonating. The higher its content, the lower the rate of carbonation; hence, the control dosing with Portland cement without additions presented an average depth of the carbonation similar or less than the other dosages, thus being more resistant to carbonation. Moreover, they have a higher alkaline reserve from alkaline oxides which, in water, produce sodium hydroxides and potassium, strong bases that have a high pH, close to 14. Concretes with diatomite have a lower alkaline reserve and produce a refinement of the pore structure. The hydration products produced by the reaction of diatomite with calcium hydroxide fill the pores, which would not only reduce the volume but, also, the size of the pores. However, a decreased alkaline reserve caused by diatomite of a pozzolanic nature may worsen carbonation.

The carbonation depth of the WineD-15 samples increases by 70%, values much higher than the rest of the concretes studied. These results are in accordance with the increase in

porosity observed in the capillary water absorption test, and are due to the organic matter content, which hinders proper setting of the concrete.

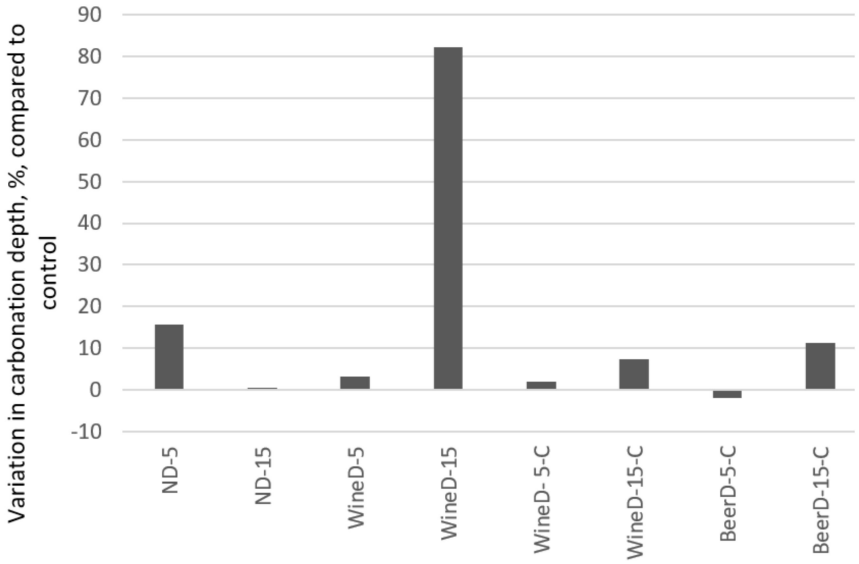



**Figure 8.** Variation in carbonation depth respect to the average value of the control concrete.

### *3.5. Resistance to Chloride Ingress*

Results obtained from the chloride ingress test (AASHTO T-259) for different concretes are presented in Table 4 and Figure 9. This method is very useful for the direct comparison of different types of concrete regarding their resistance to chloride ingress.

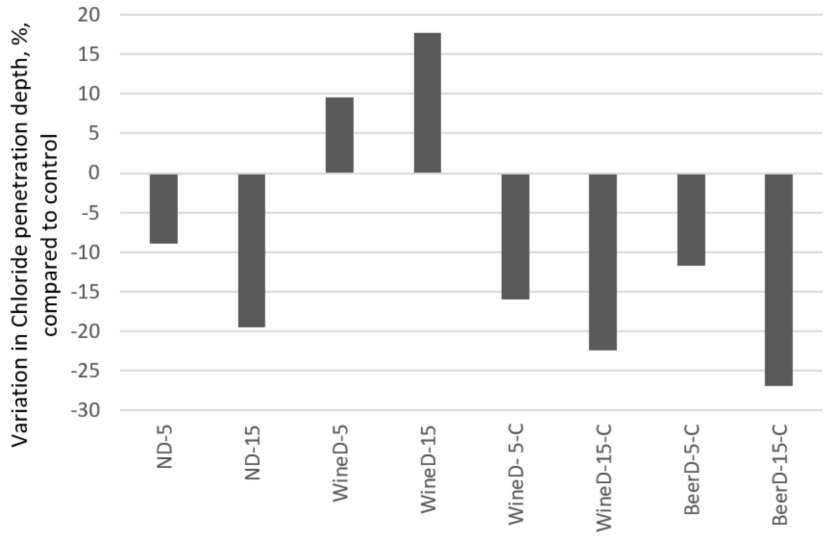



**Figure 9.** Variation in chloride penetration depth regarding the average value of the control concrete.

Generally, with the exception of samples using WineD, the use of natural and recycled calcined diatomites produces concretes with a higher resistance to chloride ingress. The use of additions, as has already been shown, increases resistance to chloride ingress, not only owing to the decrease in porosity and pore dimensions but, also, due to the chemical binding ability provided by the additions [31]. The chemical binding effect is clearly visible in ND-5 samples. These samples have a higher porosity, and, if there was no effect on the retention of chlorides due to the use of diatomite as an addition, the chloride ion would penetrate deeper and faster. Here, it is seen that the use of diatomites as an addition

provides excellent behaviour with respect to the durability of concrete regarding chloride ingress. This behaviour improves when the diatomites are calcined.

Concerning the case of diatomites recycled from wine without heat treatment, results are in accordance with those observed in both the capillary water absorption test and the carbonation depth test. The chloride depth of the WineD samples increases significantly, especially in WineD-15. Therefore, the use of recycled diatomites from the wine industry without heat treatment should only be used in non-aggressive environments when the percentage of substitution is higher than 5%, or in non-reinforced concrete.

## 4. Conclusions

According to the results presented and the discussion made in this study, the following conclusions can be drawn:

- Generally, the use of natural and recycled calcined diatomites as an addition to precast concrete improves the mechanical properties obtained by an up to 15% substitution. This improvement is more pronounced in the case of calcined recycled diatoms due to the fact that the thermal treatment increases the pozzolanic activity.
- The capillary water absorption of concrete is reduced when 15% of natural and recycled calcined diatomites are used to replace cement. The use of diatomites generates a refinement in the pore network.
- The resistance to carbonation does not improve when using diatomites as additions. The resistance to chloride ingress improves substantially when using the natural and recycled calcined diatomites. This behaviour is greater in the case of calcined diatomites.
- The use of recycled diatomites from the wine industry without heat treatment produces a decrease in mechanical and durability properties when the percentage of the substitution used is higher than 5%. Using 5%, concretes with similar properties to conventional ones are obtained. Therefore, the use of this type of recycled diatomite without heat treatment should only be used in non-aggressive environments when the percentage of substitution is higher than 5%, or in non-reinforced concrete.
- Experimental studies indicate that concretes with recycled diatomites have significant potential when considering a sustainable construction material, hence also providing a cleaner production solution for the food industry.
- Under the studied conditions it is possible to manufacture at industrial scale, precast elements with natural and recycled diatomites with improved mechanical and durability properties. Regarding the commercialization of these recycled products, it is recommended to control the organic matter content of the diatomites or to carry out a thermal treatment to ensure their quality.

**Author Contributions:** C.R., I.M., P.P. and F.B. performed the experiments, C.R. and I.M. wrote the paper, and it was supervised by C.P., with important contributions to the results analysis. The experimental design was carried out in a collaborative way among all authors. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Centro para el Desarrollo Tecnológico Industrial (CDTI), grant number IDI-20140228.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** Authors of this study would like to thank the Centro para el Desarrollo Tecnológico Industrial (CDTI) for financing the project IDI-20140228. In this study BORTUBO S.A. and the Centro Tecnológico de la Construcción de la Región de Murcia (CTCON) have participated. In the same way, we would like to thank the collaboration provided by the company CEKESA S.A.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References


1. Gartner, E.M.; Macphee, D.E. A physico-chemical basis for novel cementitious binders. *Cem. Concr. Res.* **2011**, *41*, 736–749. [CrossRef]
2. FICEM Infome Estadístico 2018: Cifras de la industria del cemento. *Cem. Concreto Iberoam. y el Caribe* **2018**, *5*, 8–12. Available online: http://ficem.org/estadisticas/informe-estadistico/ (accessed on 1 February 2021).
3. International Energy Agency (IEA) and World Business Council for Sustainable Development (WBCSD). *Cement Technology Roadmap 2009-Carbon Emissions Reductions up to 2050*; IEA: Paris, France, 2009.
4. Holcim. Available online: http://www.holcim.com/en/sustainable/environment/co2-reduction.html (accessed on 1 February 2021).
5. AENOR. *EN 197-1:2011 Part 1: Composition, Specifications and Conformity Criteria for Common Cements*; AENOR: Madrid, Spain, 2011.
6. Vegas, I.; Gaitero, J.J.; Urreta, J.; García, R.; Frías, M. Aging and durability of ternary cements containing fly ash and activated paper sludge. *Constr. Build. Mater.* **2014**, *52*, 253–260. [CrossRef]
7. Irassar, E.F.; Bonavetti, V.L.; Menéndez, G. Cementos con material calcáreo: Formación de thaumasita por ataque de sulfatos. *Rev. la Constr.* **2010**, *9*, 63–73. [CrossRef]
8. Rodríguez, C.; Sánchez, I.; Miñano, I.; Benito, F.; Cabeza, M.; Parra, C. On the possibility of using recycled mixed aggregates and GICC thermal plant wastes in non-structural concrete elements. *Sustainability* **2019**, *11*, 633. [CrossRef]
9. Crangle, R.D.; Diatomite, U.S. Commodity Summaries. *Geol. Surv. Miner.* **2014**, *2013*, 52–53.
10. Ediz, N.; Bentli, I.; Tatar, I. Improvement in filtration characteristics of diatomite by calcination. *Int. J. Miner. Process.* **2010**, *94*, 129–134. [CrossRef]
11. Ergün, A. Effects of the usage of diatomite and waste marble powder as partial replacement of cement on the mechanical properties of concrete. *Constr. Build. Mater.* **2011**, *25*, 806–812. [CrossRef]
12. Kastis, D.; Kakali, G.; Tsivilis, S.; Stamatakis, M.G. Properties and hydration of blended cements with calcareous diatomite. *Cem. Concr. Res.* **2006**, *36*, 1821–1826. [CrossRef]
13. Degirmenci, N.; Yilmaz, A. Use of diatomite as partial replacement for Portland cement in cement mortars. *Constr. Build. Mater.* **2009**, *23*, 284–288. [CrossRef]
14. Yilmaz, B.; Ediz, N. The use of raw and calcined diatomite in cement production. *Cem. Concr. Compos.* **2008**, *30*, 202–211. [CrossRef]
15. Krajči, L.; Kuliffayová, M.; Janotka, I. Ternary cement composites with metakaolin sand and calcined clayey diatomite. *Procedia Eng.* **2013**, *65*, 7–13. [CrossRef]
16. Stamatakis, M.G.; Fragoulis, D.; Csirik, G.; Bedelean, I.; Pedersen, S. The influence of biogenic micro-silica-rich rocks on the properties of blended cements. *Cem. Concr. Compos.* **2003**, *25*, 177–184. [CrossRef]
17. Fragoulis, D.; Stamatakis, M.G.; Papageorgiou, D.; Chaniotakis, E. The physical and mechanical properties of composite cements manufactured with calcareous and clayey Greek diatomite mixtures. *Cem. Concr. Compos.* **2005**, *27*, 205–209. [CrossRef]
18. Ahmadi, Z.; Esmaeili, J.; Kasaei, J.; Hajialioghli, R. Properties of sustainable cement mortars containing high volume of raw diatomite. *Sustain. Mater. Technol.* **2018**, *16*, 47–53. [CrossRef]
19. Ünal, O.; Uygunoğlu, T.; Yildiz, A. Investigation of properties of low-strength lightweight concrete for thermal insulation. *Build. Environ.* **2007**, *42*, 584–590. [CrossRef]
20. Rodríguez, C.; Miñano, I.; Aguilar, M.Á.; Ortega, J.M.; Parra, C.; Sánchez, I. Properties of concrete paving blocks and hollow tiles with recycled aggregate from construction and demolition wastes. *Materials* **2017**, *10*, 1374. [CrossRef]
21. Xu, S.; Wang, J.; Jiang, Q.; Zhang, S. Study of natural hydraulic lime-based mortars prepared with masonry waste powder as aggregate and diatomite/fly ash as mineral admixtures. *J. Clean. Prod.* **2016**, *119*, 118–127. [CrossRef]
22. 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. *Constr. Build. Mater.* **2016**, *114*, 492–498. [CrossRef]
23. AENOR. *EN 12350-2:2020 Testing Fresh Concrete—Part 2: Slump Test*; AENOR: Madrid, Spain, 2020.
24. AENOR. *EN 12390-3:2020 Testing Hardened Concrete Part 3: Compressive Strength of Test Specimens*; AENOR: Madrid, Spain, 2020.
25. AENOR. *EN 1916:2008 Concrete Pipes and Fittings, Unreinforced, Steel Fibre and Reinforced*; AENOR: Madrid, Spain, 2008.
26. AENOR. *UNE 83982:2008 Concrete Durability. Test Methods. Determination of the Capillar Suction in Hardened Concrete. Fagerlund Method*; AENOR: Madrid, Spain, 2008.
27. AASHTO. *Resistance of Concrete to Chloride Ion Penetration*; American Association of State Highway and Transportation Officials: Washington, WA, USA, 2009; pp. 24–26.
28. AENOR. *UNE 83993-2:2013 Durability of Concrete. Test Method. Measurement of Carbonation Penetration Rate in Hardened Concrete. Part 2: Accelerated Method*; AENOR: Madrid, Spain, 2013.
29. Gerengi, H.; Kocak, Y.; Jazdzewska, A.; Kurtay, M.; Durgun, H. Electrochemical investigations on the corrosion behaviour of reinforcing steel in diatomite- and zeolite-containing concrete exposed to sulphuric acid. *Constr. Build. Mater.* **2013**, *49*, 471–477. [CrossRef]

30. Sarıdemir, M.; Çelikten, S.; Yıldırım, A. Mechanical and microstructural properties of calcined diatomite powder modified high strength mortars at ambient and high temperatures. *Adv. Powder Technol.* **2020**, *31*, 3004–3017. [CrossRef]
31. Ortega, J.M.; Sánchez, I.; Climent, M.A. Durability related transport properties of OPC and slag cement mortars hardened under different environmental conditions. *Constr. Build. Mater.* **2012**, *27*, 176–183. [CrossRef]