applied sciences

MDPI

Article

Assessment of Lightweight Concrete Properties with Zinc Oxide Nanoparticles: Structural and Morphological Analyses

Ana Silvia Gonzalez Garcia [1,*], Luis Tomas Silva Klein [1], Victor Vega Martinez [2], Mar Alonso Martinez [1] and Juan José del Coz-Díaz [1]

[1] GICONSIME Research Group, University of Oviedo, 33204 Gijón, Spain; silvaluis@uniovi.es (L.T.S.K.); alonsomar@uniovi.es (M.A.M.); juanjo@constru.uniovi.es (J.J.d.C.-D.)
[2] Laboratory of Nanoporous Membranes, Scientific-Technical Services of the University of Oviedo, Campus El Cristo s/n, 33006 Oviedo, Spain; vegavictor@uniovi.es
* Correspondence: gonzalezgana@uniovi.es

Abstract: In recent decades, the use of nanotechnology has increased in many disciplines. Specifically, in the concrete industry, nanotechnology has been used to develop more eco-efficient solutions. There is a rapidly growing interest in using nanoparticles in concrete to tackle environmental impacts. Among the nanoparticles investigated, zinc oxide (ZnO) shows great potential because of its material properties, such as reactivity, non-toxicity, a hard and rigid structure, photocatalytic and photoluminescence properties, and chemical, electrical, and thermal stabilities. This paper focuses on the analysis of the effect of ZnO nanoparticles in lightweight concrete at different concentrations (0.5, 1, 1.5, and 2.0 wt%) using two different methods including (i) addition and (ii) partial substitution for cement. Mechanical properties are determined by compressive strength tests. Chemical and morphological characterization is performed using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy. This study reveals that an increase in the percentage of ZnO nanoparticles as a substitute for cement directly decreases the compressive strength of lightweight concrete. For ZnO nanoparticles in the addition method, compressive strength is 10% lower than in the control specimens. However, the conclusions indicate constant compressive strength for all ZnO nanoparticle concentrations in the addition method.

Keywords: construction industry; concrete green technology; nanotechnology; nanoparticles

Citation: Gonzalez Garcia, A.S.; Silva Klein, L.T.; Vega Martinez, V.; Alonso Martinez, M.; del Coz-Díaz, J.J. Assessment of Lightweight Concrete Properties with Zinc Oxide Nanoparticles: Structural and Morphological Analyses. *Appl. Sci.* **2024**, *14*, 4413. https://doi.org/10.3390/app14114413

Academic Editor: Syed Minhaj Saleem Kazmi

Received: 6 April 2024
Revised: 10 May 2024
Accepted: 21 May 2024
Published: 23 May 2024

1. Introduction

Nanotechnology is the manipulation of matter on a near-atomic scale to produce new structures, materials, and devices. This technology promises scientific advancement in many sectors such as medicine, consumer products, energy, materials, and manufacturing. Thus, nanotechnology involves understanding and controlling matter at the nanometer scale. The so-called nanoscale deals with dimensions between approximately 1 and 100 nanometers. As a result, nanomaterials are the foundation of nanotechnology.

Nobel laureate Richard P. Feynman was the first to speak about nanotechnology in 1959 during his famous lecture “There’s Plenty of Room at the Bottom” [1]. Since then, a revolution in this field has taken place, demonstrating Feynman’s ideas of manipulating matter at the nanoscale.

Nanomaterials show a distinct state of matter from the normally referred to states (solid, liquid, or gaseous state). Materials exhibit unique properties at the nanoscale that affect physical, chemical, and biological behavior. Quantum effects, surface effects, and confinement of electrons cause these properties and change the conductivity, reactivity, strength, and optical behavior of materials. The incorporation of nanoparticles into materials to create tailored properties is possible because nanotechnology allows for the modification of nanoparticles at the atomic and molecular levels [2].

Because of the versatility of nanotechnology, nanotech innovations influence many areas, including the construction industry, where nanotechnology represents a major opportunity to develop more sustainable materials for buildings and other constructions. Currently, there is a rapidly growing interest in using nanotechnology in concrete products to reduce their environmental impact, improve their sustainability, and mitigate climate change [3,4].

In this context, the tremendous potential of nanoparticles as nano-additives to concrete technology has been demonstrated. Nanoparticles have a very large specific surface area relative to their size. So, the incorporation of small quantities, less than 5 wt%, causes significant changes in the properties of concretes. In general, mechanical properties and durability have been enhanced using ultrafine size nanoparticles (<100 nm) with a very large specific surface area (SSA) [5]. The following three strategies were proposed to modify the regular properties of cement-based material:

- Nanoparticles provide a seeding surface for the deposition of hydrates and therefore facilitate the hydration of OPC and mineral admixtures.
- Nano-SiO_2 and other nano-clays increase pozzolanic reactivity, thus increasing the production of cementitious phases, most notably, C-S-H.
- Nanoparticles fill gaps among larger particles and modify nano and micro-scale density.

There are also limitations in the use of nanoparticles in cement-based materials. The main limitations are the following:

- The high cost of nanoparticles in comparison with other concrete components.
- Changes in the flowability and set times of OPC products, although this may be a benefit in some applications.
- High variability in OPC products with nanoparticles.

In general terms, wide-range variability has been appreciated in the incorporation of nanoparticles into cement-based material [5].

Nano-SiO_2 is strongly recommended for several applications because it improves early strength, reduces porosity, and enhances the corrosion resistance of modified concrete composites [6]. Most mixed cement-based materials with nanoparticles enhance strength performance, but it was seen that high percentages of nanoparticles may negatively affect the mechanical properties and durability of concrete. These inconveniences were associated with the difficulty of dispersion and the formation of weak spots in the matrix [6]. Previous works revealed that the careful use of nanoparticles as additives may be a novel strategy to enhance the micro- and nano-scale structure of cement-based materials. So, more deep research works are needed to develop a clear understanding of the effect of nanoparticles on OPC materials [5,6].

Some studies provide results indicating the performance of cement-based materials using nano-Al_2O_3. Diffusivity and permeability are lower than control mixtures with no additives. The compressive strength of mixtures with nano-alumina at 28 days is also discussed. Nano-Al_2O_3 improves the contact structure in the interface between cement, creating a stronger bond and reducing cracks [7]. Other research works report that nano-Al_2O_3 modifies the concrete microstructure, mainly the pore structure and interstitial transition zone, increasing the modulus of elasticity and improving compressive and bending strength [8].

The single and combined effects of nanoparticles on cement-based materials were also analyzed by other authors [9]. It was seen that the amount and type of nanoparticles had a significant influence on the fresh and hardened cement mortars studied. The combination of nanoparticles had negative effects on the physical and mechanical properties of the mortars.

Titanium oxide (TiO_2) nanoparticles are well known as a good additive to improve building sustainability and are widely used nano-additives in cement-based materials. Titanium oxide (TiO_2) nanoparticles exist in three different polymorphs including rutile, anatase, and brookite. Rutile and anatase are commonly used in the construction industry among other industries. Their effect is mainly related to the acceleration of the hydration process, an improvement in resistance, self-cleaning properties, and CO_2 uptake [10,11].

In this context, several novel nanomaterials have been explored as good additives to improve building sustainability, including nano-ZnO. Nano-ZnO is a by-product material from the zinc manufacturing industry. It is identified as a promising material because of its unique properties such as low cost, environmental benefits, and photocatalytic performance. Thus, some studies show that the incorporation of ZnO resulted in the contrary effect of a remarkable delay in the hydration process [12,13]. Nano-ZnO has a wide range of applications such as in chemical sensors, the biomedical sector, solar cells, photocatalysis, and the construction field [14]. Recent research has assessed the effect of ZnO on High-Performance Concrete (HPC) [15], concrete block pavements [12], and alkali-activated slag (AAS) [16].

In the construction industry, nano-ZnO has been assessed as a suitable alternative to TiO_2, although a few studies have compared the effectiveness of ZnO and TiO_2 [5,15,17]. Both nanoparticles, individually and combined, are used as nano-additives to enhance photocatalytic properties [15]. Previous studies reported the effect of ZnO nanoparticles on the hydration of Portland cement [15,17]. Even a very low percentage of ZnO incorporation retards the hydration of cement by forming other compounds such as $Zn(OH)_2$ or $Zn_2Ca(OH)_6{\cdot}H_2O$. The formation of $Zn(OH)_2$ is responsible for the hydration delay and an increment in pH at the initial setting time of regular concrete [18] $Zn(OH)_3{}^-$ and $Zn(OH)_4{}^{2-}$ do not influence cement hydration, but they contribute to forming Zn silicate, which is transformed into calcium zincate. Tests on normal concrete using ordinary Portland cement (OPC) incorporating percentages of 1% and 3% of ZnO showed a reduction of 30% in compressive strength [19]. However, it was seen that ZnO increased the durability of concrete in marine environments with high Cl^- concentrations [18].

Recent research studies have analyzed the influence of small additions of ZnO nanoparticles in the mechanical properties of cement-based materials [5,18,20]. However, to the knowledge of the authors, there are no studies about the effect of ZnO nanoparticles on lightweight concrete (LWC).

LWC is an adequate material to improve the sustainability of the construction industry because of its versatile properties (density below 2000 kg/m^3, porosity, recyclability, etc.) [21]. LWC use has been of great interest in recent years for many structures, such as off-shore structures, bridges, and large building roofs [22]. So, the lightness of LWC and its thermal properties make it an excellent solution for creating more sustainable materials and dealing with climate change [23]. The lightness of LWC reduces gas emissions from transportation, material extraction, civil construction, and building processes (auxiliary systems for building and supporting) [23]. The great thermal performance of LWC makes it a suitable material for energy-efficient solutions in buildings. Although LWC presents eco-friendly advantages, its environmental benefits may be enhanced by using nanotechnology, and for this, it is necessary to increase our understanding by analyzing the effect of small additions of ZnO nanoparticles. The broader scope of this research is to study the effect of ZnO nanoparticles on the performance of lightweight concrete to determine its applicability in sustainable construction and more resilient infrastructures. Other authors have studied the effect of nano-SiO_2 on the performance of lightweight concrete [24]. However, the assessment of the performance of LWC with ZnO nanoparticles is still outstanding.

Key factors to successfully incorporate ZnO nanoparticles into LWC are the incorporation method, the manufacturing process, and the effect of ZnO nanoparticles on the compressive strength of LWC.

This work designs new types of lightweight concrete (LWC) by incorporating nano-ZnO in two ways, as an additive and as a substitute for cement. The effect of ZnO incorporation in the curing process and mechanical properties is assessed.

Samples with four different percentages of ZnO additives were tested to evaluate the influence of nanoparticles on the compressive strength of the LWC. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) was used to characterize the LWC morphologically. The incorporation of ZnO nanoparticles into lightweight concrete has a direct effect on its mechanical behavior. This study reveals that an increase in the percentage of ZnO nanoparticles as a substitute for cement significantly decreases the compressive strength of lightweight concrete. However, the behavior is different for mixtures where ZnO nanoparticles are incorporated by the addition method. The use of these nanoparticles as additives in LWC leads to very similar compressive strengths for percentages of ZnO from 0.5 to 1.5 wt%. Although the compressive strength of the LWC is 10% lower than that of regular structural LWC, its resistance is stabilized for specific amounts of ZnO nanoparticles incorporated by the addition method. The conclusions show that different ways of incorporating nanoparticles may result in different mechanical responses for percentages of ZnO from 0 to 2 wt%.

2. Materials and Methods

2.1. Lightweight Concrete (LWC) Mixtures

The complete set of experimental processes to fabricate the different samples is schematized in Figure 1a–d. First, zinc oxide nanoparticles were mixed with a dry mixture. Consequently, water was added, and the saturated course aggregate was incorporated to fabricate fresh LWC (Figure 1a). After that, the molds were filled with fresh LWC, and the specimens were unmolded after 24 h at room temperature (Figure 1b). Following this, the samples were immersed in water at 20 °C for 35 days during the curing process (Figure 1c). Finally, the specimens were tested for compression until they failed after 35 days (Figure 1d).

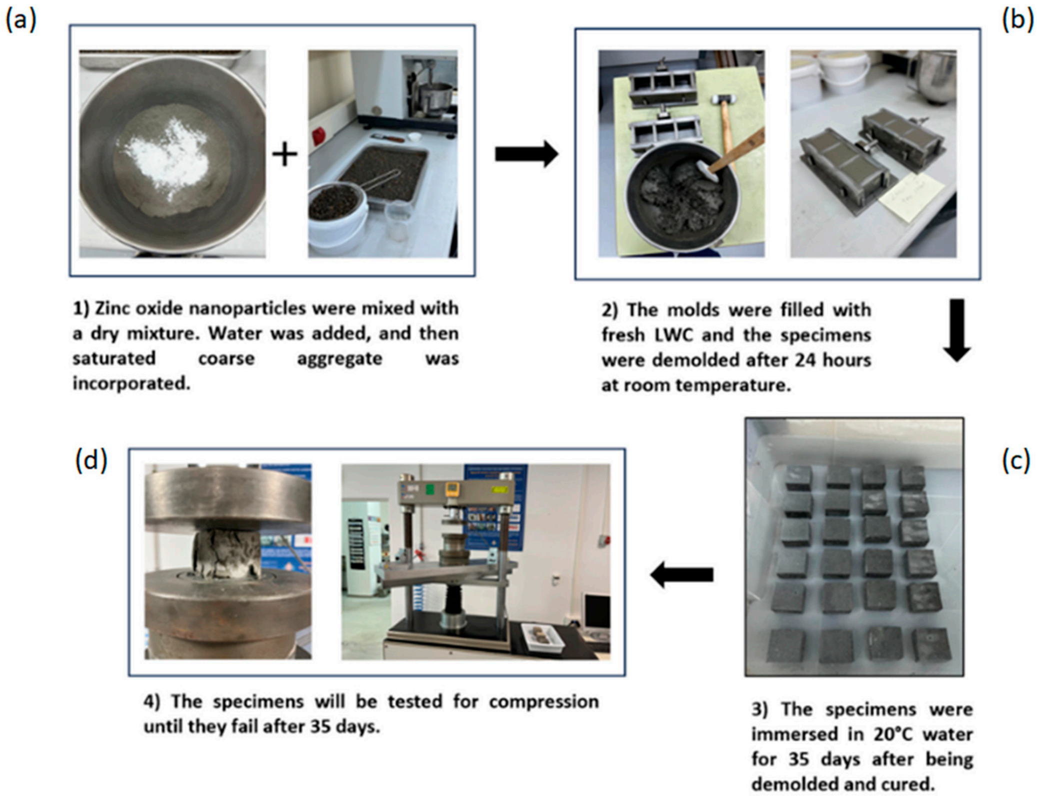


Figure 1. Schematic picture of the complete experimental process: (**a**) fabrication of fresh LWC, (**b**) molds filled with fresh LWC and unmolded after 24 h at room temperature, (**c**) immersion of the specimens in water at 20 °C for 35 days to cure them, and (**d**) testing of specimens by compressive strength tests.

The reference mixture, identified as "LWC_control", is a structural LWC made of concrete, water, fine aggregate, and lightweight aggregates combining two types of expanded clay aggregate. Cement type II A 42.5, silica sand with particle size from 0 to 2 mm and a density of 1600 kg/m^3 was used in the mixtures. The water-to-cement ratio used in the mixtures was 0.4. The coarse aggregate was lightweight expanded clay aggregate (LECA). Two sizes of lightweight aggregate were combined, including "LECA-S", with a particle size ranging from 1 to 5 mm, and "LECA-Dur", with a particle size varying from 4 to 12.5 mm. Several percentages of ZnO nanoparticles were incorporated to assess the influence of these nanoparticles in the innovative SLWC. The percentages of ZnO nanoparticles added were 0, 0.5, 1, 1.5, and 2.0 wt% through two methods of incorporation including (i) nanoparticle addition and (ii) nanoparticles as a cement substitute. The mixes with added nanoparticles are identified with "A-%", indicating the percentage of ZnO added. The mixes with ZnO as a cement substitute are identified as "S-%". Nine samples were manufactured in this work including the reference LWC and eight mixes of LWC with nanoparticles. To ensure the reliability of the results, six repetitions of each type of LWC were performed. The total procedure included six specimens of structural LWC with no nanoparticles; twenty-four samples of LWC with ZnO nanoparticles as an additive in four percentages (0.5%, 1%, 1.5%, and 2%); and twenty-four samples of LWC with ZnO nanoparticle as a substitute for cement in four percentages (0.5%, 1%, 1.5%, and 2%). So, to assess the effect of ZnO nanoparticles on LWC, fifty-four specimens were manufactured. The specimens were cube-shaped and 50 mm × 50 mm × 50 mm in size following ASTM C-109 [25]. The LWC mixtures were designed based on previous works by the authors of [26]. Table 1 shows the proportions of each type of LWC.

Table 1. LWC mixtures.

Mix	Cement (g)	Sand (g)	Coarse Aggregate (Leca-Dur) (g)	Coarse Aggregate Leca-S (g)	Water (g)	ZnO (g)
LWC_control	338.43	425.49	61.57	63.78	135.37	0
Zn-S-0.5	336.74	425.49	61.57	63.78	135.37	1.69
Zn-S-1.0	335.04	425.49	61.57	63.78	135.37	3.38
Zn-S-1.5	333.35	425.49	61.57	63.78	135.37	5.08
Zn-S-2.0	331.66	425.49	61.57	63.78	135.37	6.77
Zn-A-0.5	338.43	425.49	61.57	63.78	135.37	1.69
Zn-A-1.0	338.43	425.49	61.57	63.78	135.37	3.38
Zn-A-1.5	338.43	425.49	61.57	63.78	135.37	5.08
Zn-A-2.0	338.43	425.49	61.57	63.78	135.37	6.77

The chemical and physical properties of the used ZnO nanoparticles are shown in Tables 2 and 3.

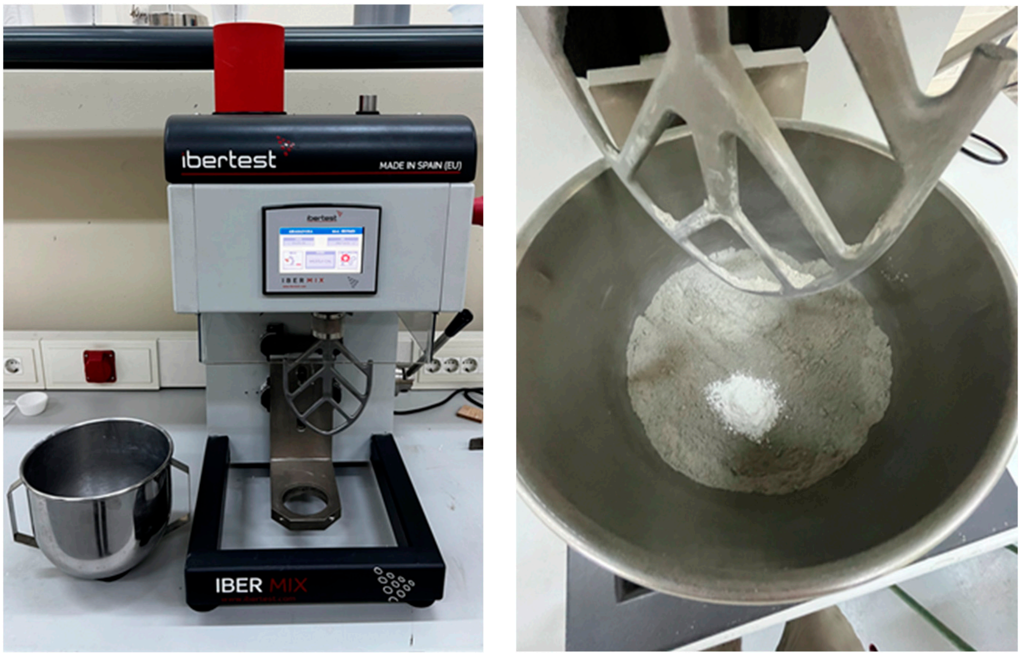
Table 2. Chemical properties.

Element	Content
Zinc oxide	≥99.9%
Pb	≤0.005%
Cd	≤0.003%
Fe	≤0.001%
Cu	≤0.001%
Weight loss at 105 °C	≤0.2%
Weight loss at 825 °C	≤0.3%
Water soluble matter	≤0.02%
Insoluble matter in triammonium liquor	≤0.01%

The manufacturing process of the LWC specimens was designed by the GICONSIME-Uniovi Research Group and mixed in their laboratories using an automatic planetary mixer. The equipment is programmable for the automatic mixing of mortars and similar materials, as shown in Figure 2.

Table 3. Physical properties.

Properties	Value
Specific surface	4.0–6.0 m^2/g
Real density	5.67 g/mL
Apparent density	0.7–1.0 g/mL
Sieve reject 45 µm	≤0.01%



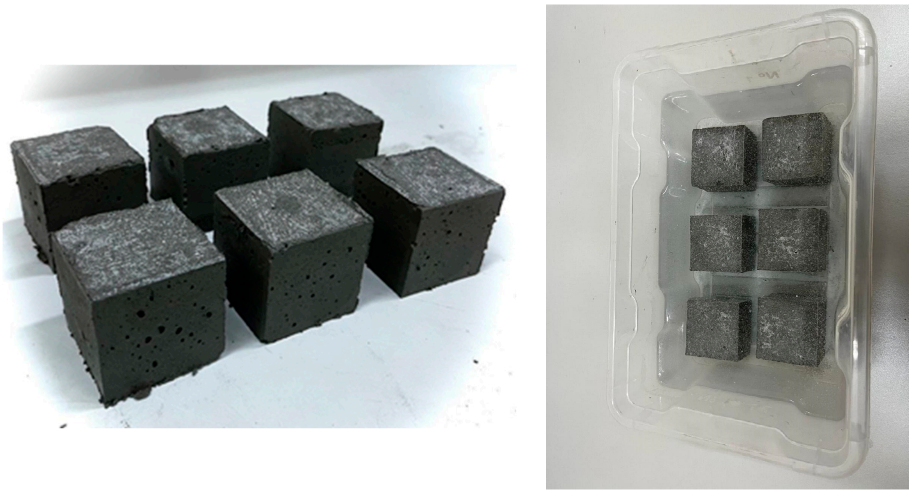
(**a**) (**b**)

Figure 2. Automatic planetary mixer: (**a**) equipment and (**b**) ZnO and cement mixture.

The mixing process was developed to obtain structural LWC with a compressive strength higher than 20 MPa. The authors developed a mixing method consisting of the following steps:

- The coarse aggregate was saturated with water for 24 h before being mixed.
- Dry cement and dry sand were mixed for 30 s at 140 rpm.
- ZnO nanoparticles were incorporated into the dry mixture and mixed for 30 s at 140 rpm.
- Water and saturated coarse aggregate were added, and all the components were mixed for 60 s at 140 rpm.
- The LWC mixtures were mixed for 90 s more at the same velocity (140 rpm)
- The fresh LWC specimens were poured into molds.

The hydration process was conducted at environment temperature during the first 24 h, and then, specimens were removed from molds, as shown in Figure 3. Following Spanish Standard UNE-EN 12390-2 [27], the specimens were submerged underwater for the curing process at a temperature ranging between 20 and 22 °C. The curing time of the LWC specimens with ZnO nanoparticles was extended to 35 days. It was seen that the incorporation of ZnO nanoparticles significantly delayed the curing process of the mixtures. In this work, it was seen that 7 extra days in this process were needed to reach structural mechanical properties.



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

Figure 3. (**a**) Cubic specimens (50 mm × 50 mm × 50 mm) of mixture type Zn-S-0.5. (**b**) The specimens submerged underwater.

2.2. Characterization Techniques

2.2.1. Compressive Strength Testing

Compressive strength was determined using a concrete compression testing machine, as shown in Figure 4. This standard equipment fulfills the technical specifications for testing machines indicated in UNE-EN 12390-4 [28].

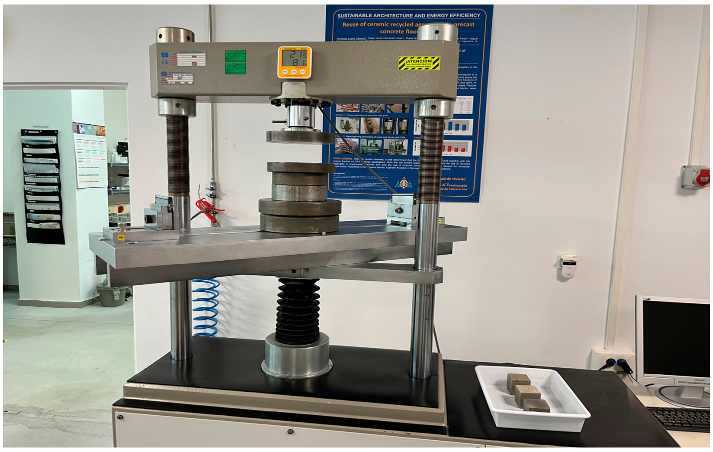


Figure 4. Compression testing machine following UNE-EN 12390-4 [25].

Compression tests were developed following standard UNE-EN 12390-3 [29]. The testing machine applied compressive strength until the final breakdown of the specimens. The testing machine was used to determine the maximum compressive load supported. Compressive strength is determined using Equation (1), according to Standard EN 12390-3, where the standard test to determine compressive strength is detailed [29].

$$f_c = \frac{F}{A_c} \quad (1)$$

where:

F: maximum compressive load.

A_c: section of the specimen where the load is applied.

Tests to determine the compressive strength of samples were performed following Spanish standard UNE-EN 12390-3 for hardened concrete characterization [29]. The specimens were loaded in a standard testing machine. A compression load was applied to the specimens, and the compressive strength was determined from the load supported until failure. In this work, cube specimens were manufactured as indicated in Section 2.1. The load-bearing surfaces were molded to be plane, ensuring the load was uniformly applied to the total surface of the specimen. The specimens were tested after the curing process at a room temperature of 21 °C. The compression load was applied at a constant rate of 0.6 MPa/s (1514.5 N/s in a square of 50 mm × 50 mm). The load was continuously increased until failure when no greater load could be supported. The testing machine used was automatically controlled.

The four cracked faces must show similar damage and cracking patterns. Satisfactory failures for cube specimens are shown in Spanish standard UNE-EN 12390-3 [29].

2.2.2. Morphological and Compositional Characterization Techniques

Morphological and compositional characterizations of ZnO nanoparticles and different samples were performed using a Scanning Electron Microscopy device (SEM, JEOL 5600, Akishima, Tokyo, Japan), equipped with an EDX microanalysis system (INCA, Oxford Instruments, Abingdon, UK).

3. Results and Discussion:

3.1. Compressive Strength Results

Figures 5 and 6 show the results of the compressive strength tests. Each curve represents the result of one specimen. Six repetitions of each mixture were performed, and valid results were drawn in different colors to identify each specimen clearly. These graphs show load–displacement curves for all the specimens tested with the same composition. Higher compressive strength is obtained when ZnO nanoparticles are added. However, the incorporation of ZnO nanoparticles as a cement substitute reduces the compressive strength of this type of LWC. Figure 6 includes only four results because two of the six specimens tested failed. Because of the heterogeneity in and high porosity of LWC, a minimum of four samples was required.

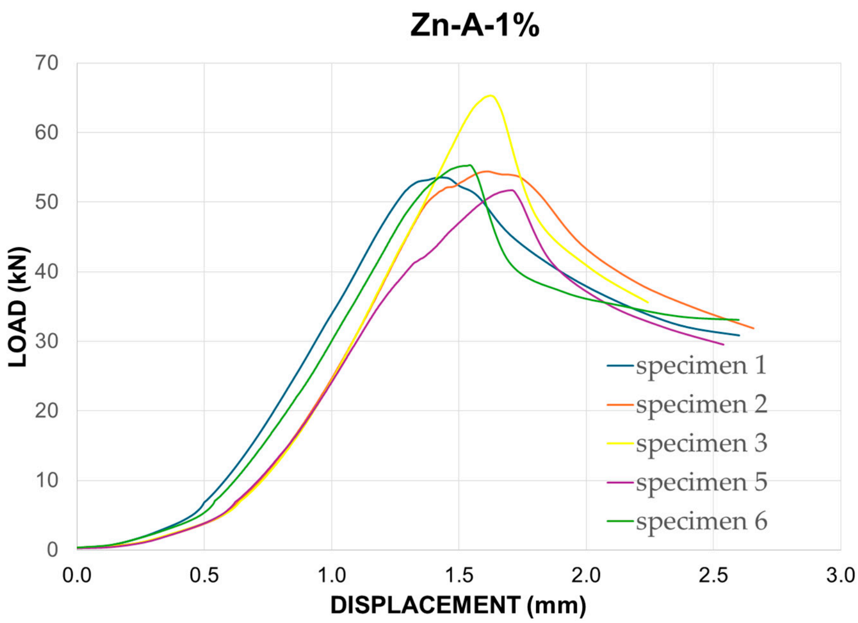


Figure 5. Force–displacement results for LWC with 1% of ZnO nanoparticles added.

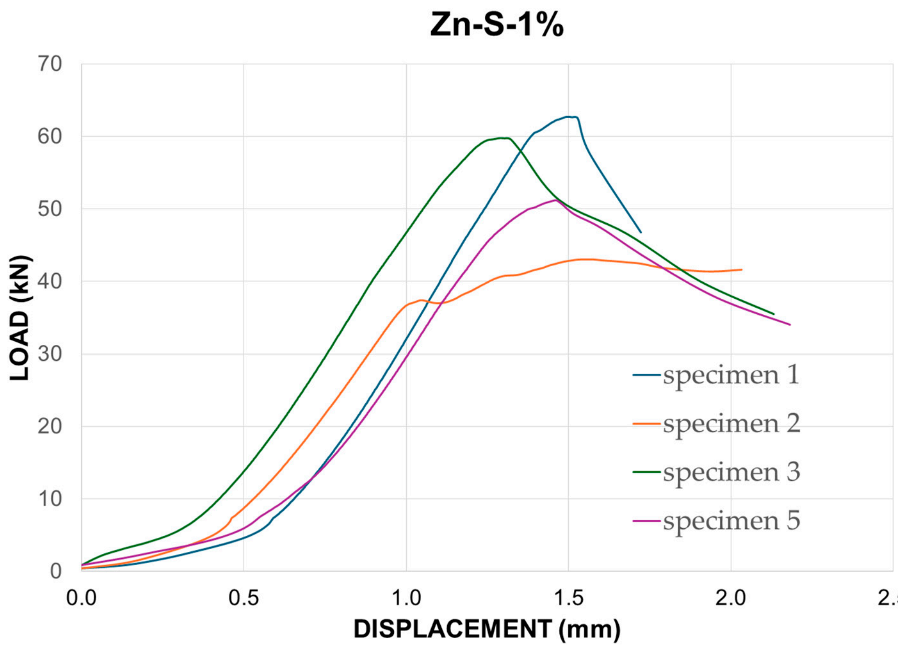


Figure 6. Force–displacement results for LWC with 1% of ZnO nanoparticles as a substitute for cement.

The average values of compressive strength were determined for each type of LWC. Table 4 includes average values for all the samples tested under compression following standard UNE-EN 12390-3 [29].

Table 4. Results of compressive strength.

Type of Mix	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Specimen 6
LWC_control	32.56	34.21	26.55	26.85	29.15	30.32
Zn-S-0.5	21.63	22.17	18.81	16.05	18.50	18.83
Zn-S-1.0	25.08	18.31	23.91	17.00	20.47	17.22
Zn-S-1.5	16.85	15.04	16.00	13.28	17.62	15.04
Zn-S-2.0	14.33	14.25	12.98	14.15	17.35	13.34
Zn-A-0.5	23.64	26.37	22.58	18.41	20.65	22.19
Zn-A-1.0	21.42	21.77	26.13	24.89	20.68	22.09
Zn-A-1.5	28.94	27.09	16.10	20.09	19.65	19.61
Zn-A-2.0	18.35	16.26	21.22	18.78	16.62	15.99

The control LWC samples reached 30 MPa in compressive strength. However, the compressive strength of the LWC with ZnO reduced for all the samples. When ZnO was incorporated as a cement substitute, compressive strength was significantly reduced. Percentages of ZnO above 1 wt% led to non-structural LWC with compressive strengths below 20 MPa. However, when ZnO was incorporated by addition, the LWC samples presented compressive strengths above 20 MPa for ZnO percentages of 1.5 wt% and below. Although the incorporation of ZnO nanoparticles reduces mechanical properties, they are still suitable for structural LWC applications with a percentage of incorporation up to 1.5 wt% as an additive. The reduction in mechanical properties when ZnO is incorporated as a cement substitute is related to the lower quantity of cement in the mixes. The lower the quantity of cement, the lower the compressive strength.

Figure 7 shows one of the samples tested in the compressive strength testing machine. Figure 7b shows satisfactory failures for the cube specimens after the test, according to standard UNE-EN 12390-3 [29].

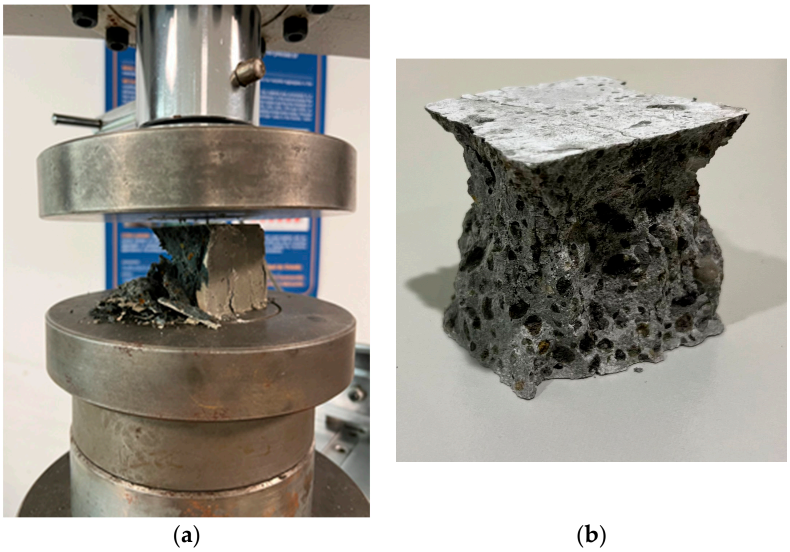


Figure 7. Specimens tested: (**a**) in the testing machine; (**b**) specimen after breakdown.

3.2. Statistical Analyses

The compressive strength results presented variability (Figure 8), so data analyses were performed to identify possible outliers. Statistical methods such as the standard deviation or boxplots are commonly used to estimate outliers in the data. The experimental data obtained in this work were statistically analyzed using the Z-score method based on the standard deviation (sd) and Tukey's methods based on boxplots [30].

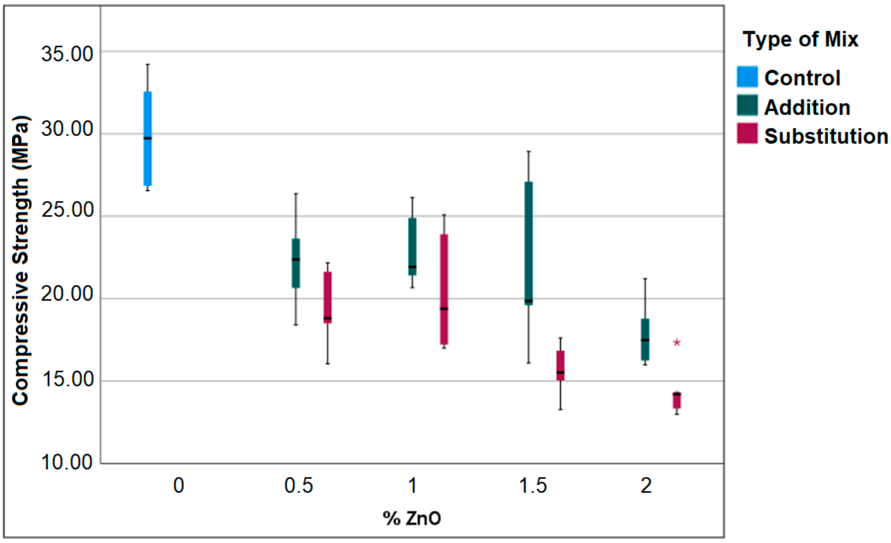


Figure 8. Compressive strength results (blue: control sample; green: ZnO as an additive; red: ZnO as a cement substitute).

3.2.1. Z-Score Method

The Z-score method uses the mean and standard deviation. The procedure is based on the following rule: if X follows a normal distribution N (μ, σ^2), then Z follows the standard normal distribution, N (0, 1). Generally, absolute values of Z-score above 3 are defined as outliers. The maximum Z-score depends on the sample size [31]. Shiffler showed that a Z-score below 3 is acceptable for a sample size equal to or greater than 10. For a sample size below 10, smaller values of the Z-score are obtained. According to Shiffler's studies, the maximum Z-score for a sample size of 5 is 1.79. In this work, a sample size of 6 was used, so the maximum Z-score was established at 2.

The Z-score value is determined using Equation (2):

$$Z_i = \frac{|x_i - \overline{x}|}{sd} \tag{2}$$

where:

x_i: experimental value of each specimen;
$\overline{x}$: mean of the sample;
sd: standard deviation of the sample.

The results obtained using the Z-score method are shown in Table 5. The experimental data have no outliers as the maximum Z-score is below 2 ($maxZ$ = 1.91).

Table 5. Z-score values.

Type of Mix	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Specimen 6
LWC_control	0.85	1.39	1.10	1.01	0.25	0.12
Zn-S-0.5	1.02	1.26	0.23	1.45	0.37	0.22
Zn-S-1.0	1.36	0.58	1.03	0.95	0.03	0.90
Zn-S-1.5	0.79	0.39	0.24	1.53	1.29	0.39
Zn-S-2.0	0.04	0.09	0.92	0.16	1.91	0.69
Zn-A-0.5	0.49	1.51	0.10	1.44	0.61	0.04
Zn-A-1.0	0.65	0.49	1.52	0.95	0.99	0.34
Zn-A-1.5	1.41	1.04	1.17	0.36	0.46	0.46
Zn-A-2.0	0.24	0.81	1.68	0.45	0.63	0.94

3.2.2. Tukey's Method

Tukey's method is a graphical tool based on a boxplot that is used to show continuous univariate data. It was used to show the compressive strength of the LWC samples. The method is based on the following steps [30]:

1. Definition of the Inter Quartile Range (IQR). IQR is the distance between the lower ($Q1$) and the upper ($Q3$) quartiles.
2. Definition of inner fences following Equations (3) and (4):

$$\text{Lower limit (inner)}: \; Q1 - 1.5\, IQR \tag{3}$$

$$\text{Upper limit (inner)}: \; Q3 + 1.5\, IQR \tag{4}$$

Although there are also outer fences, which are higher than the inner ones, the values outside of the inner fences may be considered as possible outliers. In this work, limits to identify outliers were established in the limits of inner fences. Table 6 shows the values obtained as inner fence limits using this method for all the samples. Figure 8 shows a boxplot of all the samples, showing low variability in most of the samples. Tukey's method shows that there are no outliers in the sample because all the results are inside the inner fence limits.

Table 6. Turkey's method results.

Type of Mix	Lower Limit	Upper Limit
LWC_control	20.56	38.86
Zn-S-0.5	15.04	24.46
Zn-S-1.0	9.16	31.39
Zn-S-1.5	12.64	19.03
Zn-S-2.0	12.39	15.46
Zn-A-0.5	17.53	26.89
Zn-A-1.0	17.48	28.21
Zn-A-1.5	11.04	33.92
Zn-A-2.0	12.87	22.15

3.3. Morphological and Compositional Characterizations of Samples

Figure 9 shows several SEM images and EDX. Figure 9a presents an image of ZnO nanoparticles. Figure 9b shows samples with ZnO incorporated by addition at low magnification. Figure 9c shows samples with ZnO incorporated as a partial substitute for cement at low magnification.

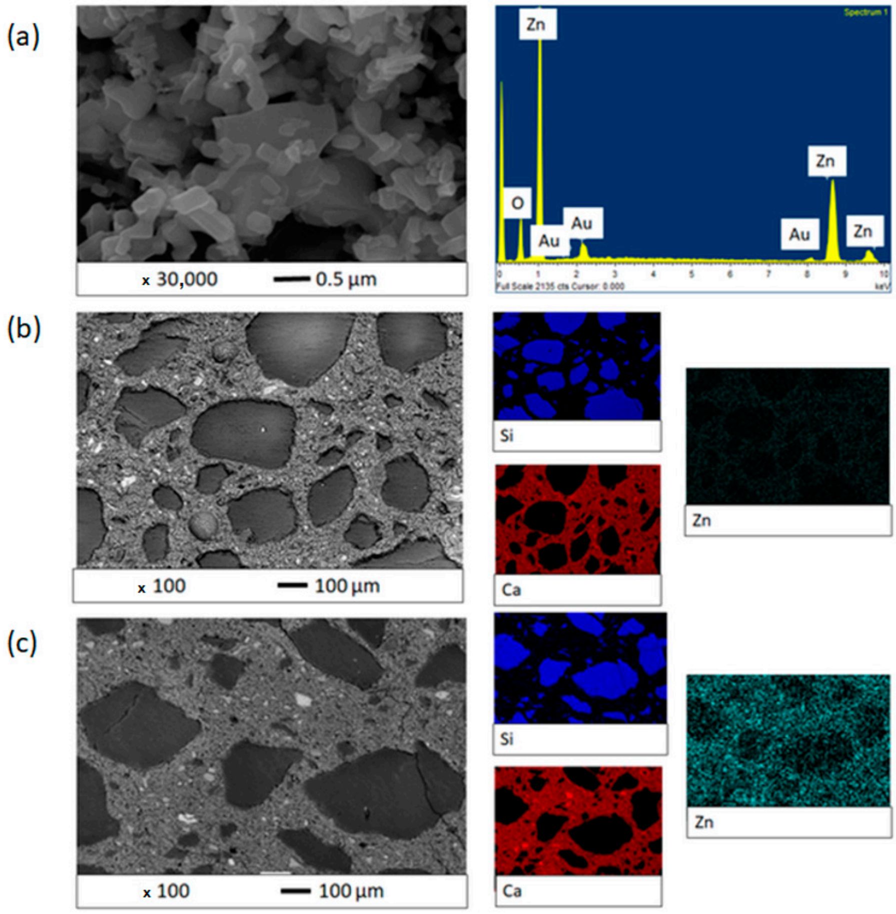


Figure 9. SEM images and EDX of ZnO nanoparticles (**a**), samples with ZnO incorporated by addition (**b**), and ZnO incorporated as a partial substitute for cement (**c**).

ZnO nanoparticles were characterized by heterogeneity in terms of shape and size, as shown in Figure 9a. The observed shapes of ZnO nanoparticles were hexagonal prisms and irregular bodies. Their length varied from 100 nm to 2000 nm. EDX study confirmed the existence of ZnO as a single phase. The presence of Au in the EDX analysis is a result of using a coating of gold to obtain a better SEM image.

Figure 9b shows micrographs of one sample with ZnO nanoparticles incorporated by addition, in this case, at 2.0 wt% ZnO nanoparticles. The mortar presented a homogeneous arrangement of pores. Figure 9b shows the element content measured by EDX. The results showed that ZnO nanoparticles had good dispersion with no aggregation.

Figure 9c shows the micrographs of one sample fabricated by partial substitution for cement, which contains 2.0 wt% ZnO nanoparticles. A homogeneous mixture was observed. Figure 9c shows the element content measured by EDX. The results showed that ZnO nanoparticles had good dispersion with no aggregation.

4. Conclusions

This work assesses the mechanical performance of LWC with ZnO nanoparticles, as well as its morphological and chemical characteristics, using two methods of incorporation and different percentages. The conclusions of this work are the following:

- The manufacturing process developed in this work provided a very homogeneous distribution of nanoparticles in LWC.
- The use of ZnO nanoparticles delays the curing process by several days. Seven extra days are needed in this process to reach structural mechanical properties.
- The incorporation of nanoparticles as a cement substitute significantly reduces the compressive strength of LWC. Percentages of ZnO nanoparticles above 1 wt% cannot be classified as structural LWC.
- ZnO incorporation by addition provides structural LWC with a compressive strength above 20 MPa when added in percentages up to 1.5 wt%.
- There is no morphological difference between the two methods of incorporation of ZnO nanoparticles. The morphological characteristics are very similar and independent of the method of incorporation and the ratio of nanoparticle/cement.

Results of this work reveal that ZnO nanoparticles reduce the compressive strength of LWC. These nanoparticles delay the hydration, hardening, and curing process of LWC, leading to changes in the mechanical performance of LWC. Future research must focus on the incorporation of a water reducer or superplasticizer to reduce the delay of cement hydration. The effect of ZnO in lightweight concrete has a great influence on hardening, leading to a lower resistance material. The micro- and macro porosity of hardened samples of LWC are also interesting properties to determine in future work.

The results of this study reveal that incorporating ZnO nanoparticles may improve the LWC durability of structures. The incorporation of ZnO delays the hydration, hardening, and curing processes. So, it is expected that the natural carbonation process will also be delayed. Creating more durable materials with good structural performance and lightweight may be very interesting for applications such as port infrastructures or aggressive environment structures, such as offshore structures.

Author Contributions: Conceptualization, M.A.M. and J.J.d.C.-D.; methodology, M.A.M.; software, L.T.S.K.; validation, L.T.S.K., A.S.G.G. and V.V.M.; formal analysis, M.A.M.; investigation, A.S.G.G.; resources, J.J.d.C.-D.; data curation, L.T.S.K.; writing—original draft preparation, A.S.G.G.; writing—review and editing, M.A.M.; visualization, V.V.M.; supervision, J.J.d.C.-D.; project administration, M.A.M.; funding acquisition, M.A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Spanish Ministry of Science and Innovation, TED2021-131976B-I00 and PID2021-128056OA-I00.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors thank the company Asturiana de Zinc from Glencore for their support of this research by providing ZnO nanoparticles as one of their industrial by-products.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Feynman, R. There's plenty of room at the bottom (Reprint from speech given at annual meeting of the American Physical Society). *Eng. Sci.* **1960**, *23*, 22–36.
2. Armarego, W.L.F. Nanomaterials. In *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, UK, 2022; pp. 586–630. [CrossRef]
3. Sanchez, F.; Sobolev, K. Nanotechnology in concrete—A review. *Constr. Build. Mater.* **2010**, *24*, 2060–2071. [CrossRef]
4. Federowicz, K.; Techman, M.; Sanytsky, M.; Sikora, P. Modification of Lightweight Aggregate Concretes with Silica Nanoparticles—A Review. *Materials* **2021**, *14*, 4242. [CrossRef] [PubMed]
5. Reches, Y. Nanoparticles as concrete additives: Review and perspectives. *Constr. Build. Mater.* **2018**, *175*, 483–495. [CrossRef]
6. Huseien, G.F. A Review on Concrete Composites Modified with Nanoparticles. *J. Compos. Sci.* **2023**, *7*, 67. [CrossRef]

7. Farzadnia, N.; Abang Ali, A.A.; Demirboga, R. Characterization of high strength mortars with nano alumina at elevated temperatures. *Cem. Concr. Res.* **2013**, *54*, 43–54. [CrossRef]
8. Iskra-Kozak, W.; Konkol, J. The Impact of Nano-Al2O3 on the Physical and Strength Properties as Well as on the Morphology of Cement Composite Crack Surfaces in the Early and Later Maturation Age. *Materials* **2021**, *14*, 4441. [CrossRef]
9. Oltulu, M.; Şahin, R. Single and combined effects of nano-SiO_2, nano-Al_2O_3 and nano-Fe_2O_3 powders on compressive strength and capillary permeability of cement mortar containing silica fume. *Mater. Sci. Eng. A* **2011**, *528*, 7012–7019. [CrossRef]
10. Hamidi, F.; Aslani, F. TiO_2-based Photocatalytic Cementitious Composites: Materials, Properties, Influential Parameters, and Assessment Techniques. *Nanomaterials* **2019**, *9*, 1444. [CrossRef]
11. Gopalan, A.-I.; Lee, J.-C.; Saianand, G.; Lee, K.-P.; Sonar, P.; Dharmarajan, R.; Hou, Y.-L.; Ann, K.-Y.; Kannan, V.; Kim, W.-J. Recent Progress in the Abatement of Hazardous Pollutants Using Photocatalytic TiO_2-Based Building Materials. *Nanomaterials* **2020**, *10*, 1854. [CrossRef]
12. Bica, B.O.; De Melo, J.V.S.; Gleize, P.J.P. Photocatalytic Concrete Blocks Nanomodified with Zinc Oxide for Paving: Mechanical Performance and Microstructural Characteristics. *J. Test. Eval.* **2021**, *49*, 2860–2884. [CrossRef]
13. Liu, J.; Jin, H.; Gu, C.; Yang, Y. Effects of zinc oxide nanoparticles on early-age hydration and the mechanical properties of cement paste. *Constr. Build. Mater.* **2019**, *217*, 352–362. [CrossRef]
14. Le Pivert, M.; Poupart, R.; Capochichi-Gnambodoe, M.; Martin, N.; Leprince-Wang, Y. Direct growth of ZnO nanowires on civil engineering materials: Smart materials for supported photodegradation. *Microsyst. Nanoeng.* **2019**, *5*, 57. [CrossRef] [PubMed]
15. Amor, F.; Baudys, M.; Racova, Z.; Scheinherrová, L.; Ingrisova, L.; Hajek, P. Contribution of TiO_2 and ZnO nanoparticles to the hydration of Portland cement and photocatalytic properties of High Performance Concrete. *Case Stud. Constr. Mater.* **2022**, *16*, e00965. [CrossRef]
16. Tan, J.; Sierens, Z.; Vandevyvere, B.; Dan, H.; Li, J. Zinc oxide in alkali-activated slag (AAS): Retardation mechanism, reaction kinetics and immobilization. *Constr. Build. Mater.* **2023**, *371*, 130739. [CrossRef]
17. Goyal, R.; Verma, V.K.; Singh, N. Effect of nano TiO_2 & ZnO on the hydration properties of Portland cement. *Mater. Today Proc.* **2022**, *65*, 1956–1963. [CrossRef]
18. Zhang, M.; Du, L.; Li, Z.; Xu, R. Durability of marine concrete doped with nanoparticles under joint action of Cl- erosion and carbonation. *Case Stud. Constr. Mater.* **2023**, *18*, e01982. [CrossRef]
19. Soto-Felix, M.; Baldenebro-Lopez, F.J.; Carreño-Gallardo, C.; Herrera-Ramirez, J.M. Hybrid Cements with ZnO Additions: Hydration, Compressive Strength and Microstructure. *Molecules* **2022**, *27*, 1278. [CrossRef] [PubMed]
20. Garg, R.; Garg, R. Effect of zinc oxide nanoparticles on mechanical properties of silica fume-based cement composites. *Mater. Today Proc.* **2021**, *43*, 778–783. [CrossRef]
21. *CEN EN 206: 2013*; Concrete—Specification, Performance, Production and Conformity. European Committee for Standardization: Brussels, Belgium, 2013.
22. Iyer, N.R. An overview of cementitious construction materials. In *New Materials in Civil Engineering*; Elsevier: Amsterdam, The Netherlands. [CrossRef]
23. Bozorgmehr Nia, S.; Nemati Chari, M. Applied development of sustainable-durable high-performance lightweight concrete: Toward low carbon footprint, durability, and energy saving. *Results Mater.* **2023**, *20*, 100482. [CrossRef]
24. Wang, X.F.; Huang, Y.J.; Wu, G.Y.; Fang, C.; Li, D.W.; Han, N.X.; Xing, F. Effect of nano-SiO_2 on strength, shrinkage and cracking sensitivity of lightweight aggregate concrete. *Constr. Build. Mater.* **2018**, *175*, 115–125. [CrossRef]
25. *ASTM C109*; Standard Test Method for Compressive Strength of Hydraulic Cement Mortars. ASTM International: West Conshohocken, PA, USA, 2009; Volume 80.
26. Rabanal, F.P.Á.; del Coz Díaz, J.J.; Alonso-Martinez, M.; Martínez, J.E.M. Thermal and structural optimization of lightweight concrete mixtures to manufacture composite slabs. In Proceedings of the International Conference on Mechanical Models in Structural Engineering—CMMoST, Alicante, Spain, 23–25 October 2019; pp. 657–667.
27. *EN 12390-2:2020*; Testing Hardened Concrete. Part 2: Making and Curing Specimens for Strength Tests. European Committee for Standardization: Brussels, Belgium, 2020.
28. *EN 12390-4:2019*; Testing Hardened Concrete Compressive Strength. Specification for Testing Machines. European Committee for Standardization: Brussels, Belgium, 2019.
29. *EN 12390-3*; Testing Hardened Concrete. Part 3: Compressive Strength of Test Specimens. European Committee for Standardization: Brussels, Belgium, 2019.
30. Seo, S. A Review and Comparison of Methods for Detecting Outliers in Univariate Data Sets. Master's Thesis, University of Pittsburgh, Pittsburgh, PA, USA, 2006.
31. Shiffler, R.E. Maximum Z Scores and Outliers. *Am. Stat.* **1988**, *42*, 79–80. [CrossRef]