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Improving the Mechanical Properties of Mortars by the Addition of Metal-Doped Zinc Oxide Nanoparticles †

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Abstract: The evolution of construction engineering depends on the development of cementitious materials with optimized properties and lower environmental impacts, such as the preparation of mortars with higher mechanical resistance and durability. Nanotechnology is a promising area for industrial innovation, enhancing materials properties, like durability and mechanical performance. Thus, herein we prepared mortars incorporating ZnO nanoparticles and evaluated their properties. The results showed that smaller percentages of ZnO presented a better performance for consistency tests, and all samples containing ZnO showed higher mechanical resistance than the reference. Thus, suggesting the great potential of nanoparticles in optimizing the mechanical properties of mortars.

Keywords: Cementitious materials; Nanostructures; Mechanical resistance; Consistency tests.

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1. Introduction

Civil construction is considered one of the mainsprings of world urban development, which makes the materials used by this sector one of the most consumed in the world. The concept of cementitious composites is related to the range of materials made with cement. Among them, mortar stands out for its properties, performance, and versatility [1]. Mortar is basically composed of water, cement, and fine aggregates, and may contain an additive to improve a specific property. These components are fractionated in the proper proportion and mixed in order to obtain a homogeneous mass with specific characteristics, both in the fresh and hardened state, such as density, consistency, hardness, and resistance to compression [2].

However, the production of these materials has been the target of criticism due to the damage caused to the environment, mainly owing to the release of polluting phases during cement production [3].

In recent decades, researchers around the world have shown interest in the use of nanomaterials as a strategy for optimizing various materials, including civil construction materials, such as concrete and mortar, in order to increment existing knowledge about the cementitious matrix of these materials and to expand the understanding about the nanometric incorporation in these materials [4].

Among the nanomaterials incorporated in cementitious composites, nanoparticles (NPs) based on metallic oxides, such as SiO_2, Al_2O_3, Fe_2O_3, ZnO and TiO_2 stand out [5, 6]. Therefore, the objective of this work was to prepare mortars incorporating different percentages of zinc oxide nanoparticles doped with cobalt (ZnO:Co) to evaluate the properties of the mortar in the fresh and hardened states.

2. Materials and Methods

2.1. Synthesis and Characterization of ZnO:Co Nanoparticles

ZnO:Co nanoparticles were prepared by dissolving $ZnCl_2$ (2 mmol), $CoCl_2·6H_2O$ (0.10 mmol) and mercaptosuccinic acid (MSA) (8 mmol), acting as surface stabilizing agent, in 50 mL of deionized water, and the pH of the solution was adjusted, under constant stirring, to approximately 11 with a solution of NaOH (4 M). The system was maintained under constant stirring at a temperature of 80 °C for 90 min [7]. After the end of the synthesis, the colloidal suspension was frozen to promote the colloidal destabilization. After thawing at room temperature, the precipitate was purified and washed with distilled water and ethanol using a porous plate funnel for filtration. Subsequently, the material was dried in an oven for 1 h at 120 °C, followed by the calcination process of the material, in a muffle furnace for 2 h at 300 °C [8,9]. For the structural and morphological characterization of ZnO:Co NPs, X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis were performed.

The X-ray diffraction (XRD) profile of colloidal prepared ZnO:Co nanoparticles, in the range of 20° < 2θ < 100° with a step size of 0.02° and scan speed of 0.235364 °/min was obtained in Rigaku SmartLab diffractometer, using CuKα1 radiation with the wavelength of 1.54059 Å, and the accelerating voltage of 40 kV. The particle size and the microstrain have been calculated using the Average Model of Scherrer Equation [10], Equation (1), and microstrain of network [8] according with Equation (2).

$$D = \frac{K\lambda}{\beta} \cdot \frac{1}{cos\,\theta} \quad (1)$$

and

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (2)$$

where D is the size of the particle, λ is the wavelength of CuKα radiation, β is the full width at half-maximum (FWHM) intensity, and θ is the peak position.

2.2. Mortar Preparation and Characterization

The materials were used without further purification, using early strength portland cement (CP V), natural sand, and water as provided by the suppliers.

To prepare the cementitious composite, 600 g of cement and 2,400 g of natural sand were considered, and a water-cement ratio (w/c) of 0.78 was used (considering the volume of the ZnO:Co NPs suspension).

To prepare the mortar, first, the water was mixed with the solution of the nanoparticles (0.5 and 1% of ZnO:Co NPs in relation to the cement mass). Next, all the anhydrous mortar (3.0 kg) was placed in the mixer tank, overlapping layers of cement and sand. The mixer was turned on at low speed and 75% of the mixing water was added in the initial 10 s, mixing until completing the time of 30 s. The speed was changed to high and the material was mixed for a further 60 s. After this phase, the mixer was stopped for 90 s to scrape the entire internal surface and the blade, then turn the mixer on at low speed and add the rest of the water (25%) in 10 s, continuing the mixing until completing 60 s.

The mortar was characterized in triplicate through consistency tests (Flow Table) and compressive strength at 7 and 28 days.

3. Results and Discussion

3.1. Synthesis and Characterization of ZnO:Co NPs

The synthesis of Co-doped ZnO NPs using chloride salts as precursors was successfully performed. Information regarding the structural properties of ZnO:Co NPs was obtained from the analysis of X-ray diffractograms to identify the crystalline phase, estimate the NPs' average size, and determine the microstrain of the network.

The X-ray diffraction (XRD) profile of colloidal prepared ZnO:Co nanoparticles is shown in Figure 1-a. Diffraction pattern showed peaks at 31.63°, 34.28°, 36.09°, 47.41°, 56.40°, 62.69° and 67.73°, corresponding to the planes (100), (002), (101), (102), (110), (103), and (112), which matches with the stick pattern of the Joint Committee on Powder Diffraction Standards (JCPDS), having the card no. 01-080-0074 of hexagonal wurtzite structure of ZnO nanocrystals. Peaks near 45° identified with an asterisk can be attributed to impurity phases probably from CoO or Co clusters. The Table 1 shown the size estimated by Average Model of Scherrer Equation for the reflections peaks highlighted.

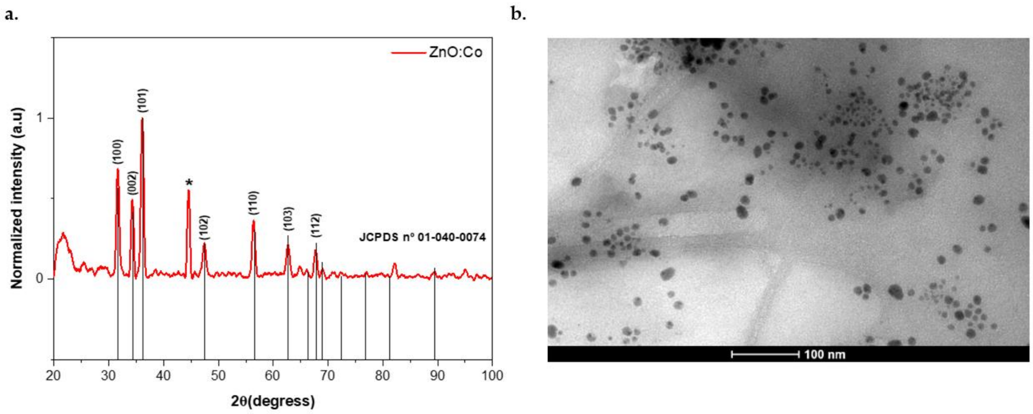

Figure 1. (a) Structural analysis of Co-doped ZnO NPs, obtained via colloidal synthesis, using chloride salts as precursors: X-ray powder diffraction patterns of ZnO and ZnO:Co. (b) TEM image of ZnO:Co NPs.

Table 1. Values of ZnO:Co crystal size extracted by the average method based in Scherrer Equation.

Reflections	Peaks position (2θ)	Size (nm)
(100)	31.63	14.36
(002)	34.28	16.38
(101)	36.09	14.44
(102)	47.41	13.85
(110)	56.40	15.80
(103)	62.69	14.94
(112)	67.73	19.03

The average size was at about 16 nm and the microstrain for each reflection was about 0.0023. The widening of the diffraction peaks may be due to the size and microstrain of the nanoparticles, possibly caused by uniform compression deformation effects due to the presence of Co^{2+} with an ionic radius smaller than Zn^{2+}, 58 Å and 60 Å, respectively, which decreases the equilibrium distances between Co^{2+} and O^{2-} in the crystal lattice of ZnO [11]. Furthermore, the presence of the stabilizing agent (MSA) influences the nucleation and growth processes of nanoparticles, favoring greater size control, resulting in smaller crystals than by more usual synthesis methods such as coprecipitation.

Morphological analyzes were carried out using the TEM technique, in which a quasi-spherical morphology was observed for the nanoparticles. Using the ImageJ Open-Source software, with a reference sample of 350 particles, was obtained an average diameter of around 9 nm, as shown in Figure 1-b.

3.2. Mortar Preparation and Characterization

The mortar preparation was successfully carried out, as observed in the consistency test (Flow Table). However, a better performance was observed in the mortar spreading for the addition of 0.5% ZnO:Co NPs when compared with the control (without NPs), as shown in Figure 2-a. By increasing the percentage of nanoparticle addition to 1% of

ZnO:Co NPs, it is possible to notice a decrease in the scattering. This fact may be related to the relationship between the surface area of the NPs and the water present in the mixture, since a greater amount of nanomaterial may have caused greater absorption of water from the mixture, decreasing its consistency [12].

The compressive strength tests were performed at 7 and 28 days. The mortars containing nanoparticles performed better than the control for mechanical strength, the samples containing 0.5% of ZnO:Co NPs performed better for compressive strength at 7 days, while samples containing 1% ZnO:Co NPs showed better values for strength at 28 days, as shown in Figure 2-b. This feat is related to the hydration process and microstructure of the cementitious matrix, as the presence of nanomaterials increases the initial hydration rate and the amount of hydrated calcium silicate gel CSH, in addition to reducing the porosity of the material [13].

a. **b.**

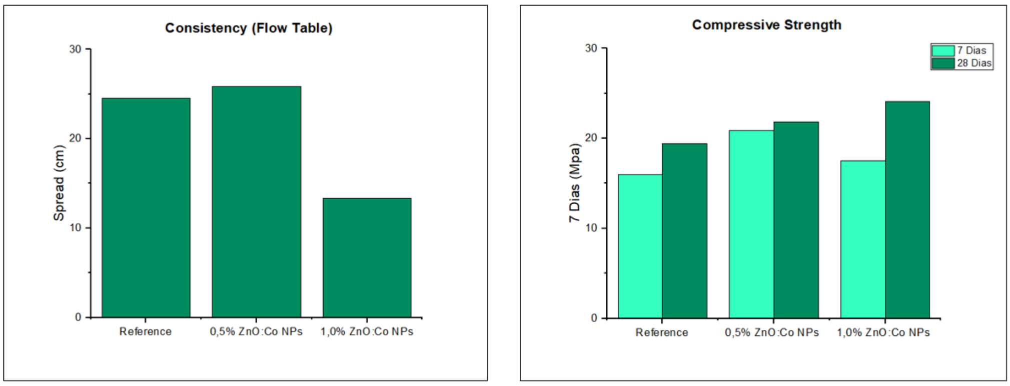

Figure 2. (a) Consistency (Flow Table) of the mortar with the addition of 0.5 and 1% of ZnO:Co NPs and (b) Compressive Strength at 7 and 28 days for the addition of 0.5 and 1% of ZnO:Co NPs.

4. Conclusion

In this work, Co-doped ZnO nanoparticles were successfully prepared in water by colloidal method. The ZnO:Co NPs were obtained in an almost spherical shape, as confirmed by the TEM, and presented X-ray diffraction peaks very similar to the reference ones. The additions of nanoparticles to the mortar were successful, and it was possible to observe an optimization of the properties of the mortar in relation to the control. The values obtained for the consistency and compressive strength tests, suggest the high potential of application of these nanomaterials in mortar as a strategy to improve its properties.

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Data Availability Statement: The data presented in this study are available in this article.

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