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Research Article

Effects of $FeNi_3$ Nanoparticles and Coal Slag on Mechanical and Durability Properties of Concrete against Acidic Environments

Hossein Rezayt Khargerdi[1], **Seyed Mojtaba Movahedifar**[1], **Alireza Motavalizadehkakhky**[2,3], **Amin Honarbakhsh**[1,4] **and Rahele Zhiani**[2,5]

[1]*Department of Civil Engineering, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*
[2]*Department of Chemistry, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*
[3]*Advanced Research Center for Chemistry, Biochemistry & Nanomaterial, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*
[4]*New Materials Technology and Processing Research Center, Department of Civil Engineering, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*
[5]*New Materials Technology and Processing Research Center, Department of Chemistry, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*

Correspondence should be addressed to Seyed Mojtaba Movahedifar; movahedi_far@yahoo.ca and Amin Honarbakhsh; amin_honarbakhsh@yahoo.com

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In recent years, natural pozzolans have been proposed as a way to improve the mechanical and biocompatible properties of concrete. This study investigated the effects of different amounts of nanoparticles, coal slag pozzolan, and their combination on the mechanical properties and durability of concrete. For each mixed design, nine cubic samples of $10 \times 10 \times 10$ cm and 30×15 cm were made and then cured in water for 28 days before being tested for compressive and tensile strength. According to the results, pozzolan at about 5% of cement weight increased the compressive strength of concrete compared to samples without pozzolan. Nanoparticles of $FeNi_3$ greatly enhanced the compressive and tensile strength of concrete in most samples containing nanoparticles. The compressive and tensile strength of 28-day concrete increased by 27% and 18%, respectively. Pozzolan (10%) and 2% of $FeNi_3$ (CP10F2) in concrete also reduced the water absorption of the samples, which can improve the durability parameters of concrete. In concrete exposed to sulfuric acid, sample CP0F2 (2% of $FeNi_3$ nanoparticles) had a positive effect on compressive strength, and samples containing 2% of $FeNi_3$ nanoparticles had higher compressive strength than those with pozzolan replacing cement. The simultaneous use of coal slag and $FeNi_3$ nanoparticles has increased the mechanical properties and durability of concrete in addition to reducing cement consumption.

1. Introduction

During cement preparation, gas and heat pollution are produced, and the volume of these pollutants can be hazardous to the environment. The cement industry produces these pollutants through chemical reactions between the materials and fuels used [1]. In Iran, because of the huge oil and gas reserves, coal and coke are not consumed in the cement industry. Natural gas, diesel, fuel oil, coal, and coke are the fuels used in the cement industry [2].

It is possible to reduce the production of pollutants in the cement industry by improving the efficiency of the production process [3]. Recently, many studies have been done in this field [4, 5]. It is necessary to find solutions to protect the environment from the emission of greenhouse gases related to cement production [6]. One of the most effective solutions and techniques is the use of pozzolans in concrete. Both environmental and economic benefits can be derived from the use of these materials. Today, the biocompatibility of concrete has been given the same importance as its other properties. Pozzolans can also improve the mechanical properties of concrete [7].

According to the ASTM-C618 standard, pozzolan is a siliceous or siliceous aluminate material that does not possess adhesive properties on its own, but when present in very fine particles near moisture at normal temperatures, it reacts chemically with calcium hydroxide and produces compounds that have cement and adhesive properties [8, 9]. From the point of view of the effect of using pozzolans on the properties of concrete, the use of pozzolanic materials increases the setting time, increases efficiency and adhesion, reduces water shedding and segregation in fresh concrete, reduces permeability, reduces porosity, increases the long-term compressive strength, and increases the concrete's resistance to chemical attacks. Moreover, these materials reduce corrosion of steel reinforcements in concretes that are exposed to chemical attacks [10].

Pozzolan improves the durability of concrete in sulfate environments [11]. Using pozzolans in concrete improves its mechanical properties, durability, and useful life [12]. Dahish et al. [13] investigated the effect of combining natural pozzolan and silica fume in cement-based mortars. Their results showed that up to 40% of cement weight can be replaced with pozzolan.

Since the use of pozzolans usually reduces the compressive strength of concrete, in order to reduce this negative effect, nanoparticles are used in concrete [14]. Nanoparticles can increase the density of particles in concrete, thereby increasing the density of nanostructures in concrete and improving its mechanical properties. Using nanoparticles to strengthen concrete has been proven [15, 16]. In addition to serving as a filler in concrete microstructures, concluded that nanosilica acts as an activator in pozzolanic reactions [17]. Nanosilica was found to increase the compressive, tensile, and bending strength of concrete [18]. According to Maheswaran et al. [19], nanosilica improves the mechanical properties and durability of concrete. According to Yang's study, nanosilica increases concrete's tensile strength and shrinkage limit [20]. As nanosilica has a very high specific surface area, it increases the amount of water used in concrete, which is why superlubricants are used in the mixing plan to prevent an increase in water–cement ratios [21].

As a result of sulfate attack, concrete structures have a shorter life expectancy. Using type 2 and 5 cement instead of type 1 cement is the most common solution to these attacks [22]. It is also possible to substitute cement with materials such as fly ash, microsilica, and natural pozzolans [23, 24]. Using natural pozzolan in self-compacting concrete increases its resistance to hydrochloric acid and sulfuric acid attacks [25]. According to Shaikh et al. [26] increasing silica nanoparticle amounts up to 2% increases compressive strength and increasing amounts decreases it.

Ahmadi et al. [27] have mentioned an increase in mechanical properties of concrete when nanoparticles are used instead of cement. It is essential to develop new cement products that maintain the mechanical properties of concrete while being biocompatible and have a lower environmental impact due to the increasing consumption of cement and its inevitable inevitability, as well as considering the dangers associated with cement production and air pollution. This study aims to determine if biocompatible materials can be used in concrete's composition without reducing its mechanical properties. In addition, pozzolanic compounds are investigated for their effect on the properties of concrete exposed to sulfuric acid.

Table 1: Results of XRF analysis of coal slag pozzolan.

Entry	Chemical composition	Percent
1	SiO_2	44.22
2	Al_2O_3	22.84
3	Fe_2O_3	19.5
4	Na_2O	1.211
5	K_2O	4.5
6	MgO	1.65
7	SO_3	2.72
8	P_2O_5	0.396
9	CaO	1.281
10	TiO_2	1.722

2. Materials and Methods

All chemicals used in the laboratory were purchased from Merck and Floka companies in high purity. This research was conducted using an infrared spectrometer (FTIR) from Elmer Perkin. A scanning electron microscope (SEM) model MIRA III was used to observe concrete structure. X-ray fluorescence (XRF) analysis is one of the most widely used analyses in industry and academic research and is included in the spectroscopic analysis category. XRF is elemental analysis. This means that it can measure the concentration of the main mineral and metal elements of the sample and other elements. XRF analysis has been used to detect the chemical composition of the coal slag pozzolan sample (Table 1). Coal slag has 10 different types of composition, most of which are related to SiO_2.

2.1. General Method to Synthesis of $FeNi_3$ Nanoparticles. 0.01 mol $FeCl_2{\cdot}4H_2O$ and 0.03 mol $NiCl_2{\cdot}6H_2O$ to 200 ml were added to distilled water, then 1 g of 6,000 MW polyethylene glycol (PEG) was added. Sodium hydroxide (NaOH) was added to the solution, and pH was controlled at $13 \leq pH \leq 12$. The suspension was treated with 5 ml of hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 80% concentration). During the reaction, room temperature was maintained for 24 hr. In addition, the pH decreases as the reaction proceeds. Using a pH meter and adding NaOH to the reaction medium, the pH was set in the range of $13 \leq pH \leq 12$. The product was washed with deionized water and dried at 70°C under vacuum [28].

2.2. Cement and Aggregate. Type II portland cement was used to make all the samples, according to ASTM C150 standard [29]. The chemical characteristics of portland cement were determined by XRF test and are presented in Table 2. There are 13 different types of compounds in this type of cement.

In general, aggregates that have a continuous granulation curve, so that some of the grain sizes in them are not too

Table 2: Specifications for Type 2 portland cement.

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	L.O.I	C_3S	C_2S	C_3A	C_4AF
62.5	21	4.6	3.9	2.9	0.45	0.5	2	1.4	54	23	5.6	12

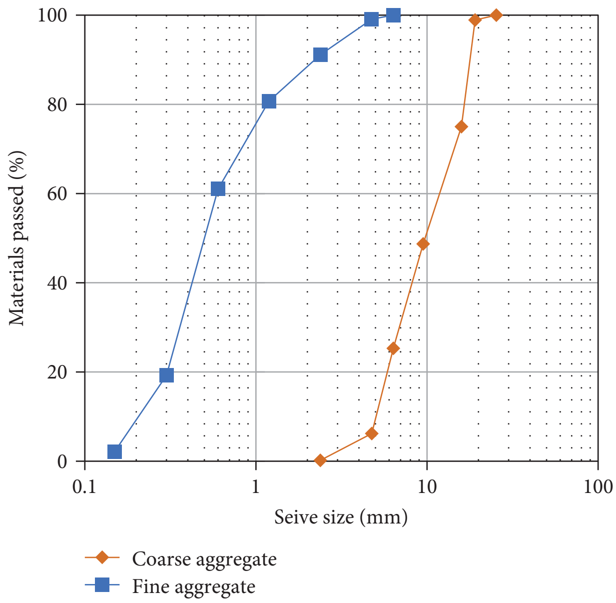


Figure 1: Aggregate granulation curve.

small or too large, bring the most satisfactory results. The aggregates used are fine and coarse washed aggregates. As shown in Figure 1, aggregates granulate at different rates. Which is in accordance with the ASTM C33 standard [30].

2.3. Mixed Design. In this study, 5%, 10%, and 15% of coal slag and 1%, 2%, and 3% of $FeNi_3$ nanoparticles were used relative to the weight of cement to investigate their effects on concrete properties. Each design consisted of three cubic samples of $10 \times 10 \times 10$ cm and three cylindrical samples of 30×15 cm. The mixing plan for the control sample can be found in Table 3.

The names of the tested samples were as follows: C: concrete, P: pozzolan, F: $FeNi_3$ nanoparticles, and the subscripts P and F indicate the replacement percentage of these materials instead of cement in terms of weight percentage of cement. A 24-hr mold curing period was followed by a 28-day curing period in the water tank, and after 28 days, the samples were removed from the water to determine their compressive strength and tensile strength.

The applied superplasticizer is liquid superplasticizer is dark brown in accordance with ASTMC1017 standards. The water-to-cement is accordance with the standard ACI318-83 [31].

To investigate whether pozzolan and $FeNi_3$ nanoparticles affect the compressive strength of concrete exposed to sulfuric acid, according to ASTM C1012 [32]. The samples were transferred to a 30% sulfuric acid solution after 28 days of curing, and their compressive strength was measured after 2 weeks. A TEMCO device model ML 802-4 B 14 was used to measure the compressive strength of the samples.

3. Results and Discussion

FTIR spectroscopy was used to determine the surface change of nanoparticles. Infrared spectroscopy of $FeNi_3$ nanoparticles was investigated in Figure 2. Fe–Ni stretching vibrations at 631, 840 cm^{-1} and O–H stretching vibrations at 3,389 cm^{-1} were observed. Other absorption peaks in the sample are due to the presence of some impurity in the raw materials of PEG or hydrazine.

SEM was used to analyze the structure of $FeNi_3$ (Figure 3). The structure and morphology of $FeNi_3$ were investigated using SEM. As you can see, $FeNi_3$ metal nanoparticles have a spherical anatomy with fixed dimensions. These nanoparticles contain spheres with a diameter of about 14–53 nm in a spherical shape, which have easy access to the upper surface. SEM photographs showed the regular arrangement of $FeNi_3$ without the formation of extra particles.

3.1. The Effect of Nanoparticles on Compressive and Tensile Strength of Concrete. Figures 4 and 5 illustrate the effect of using different percentages of $FeNi_3$ nanoparticles on the compressive and tensile strength of concrete at 7, 28, and 90 days. By replacing cement with nanoparticles, concrete's compressive and tensile strength increased, and this increase was greater in the sample with 2% of nanoparticles compared to the other samples and the control sample. Considering that in all mixing designs used in this study, only the percentage of nanoparticles and coal was different and other characteristics like water–cement ratio, superlubricant, and aggregates were considered constant, the strength reduction of samples with higher amounts of nanoparticles has 2% of nanoparticles as compared to the sample. There is a lack of sufficient water to create adhesion between particles, which occurs because the lateral surfaces of the particles increase and more water is absorbed under constant conditions.

The effect of coal slag pozzolan on compressive and tensile strength of concrete Figures 6 and 7 show how coal slag affects concrete's compressive and tensile strength. The use of pozzolan in amounts of 5% and 10% instead of cement increased the compressive and tensile strength of concrete. However, the strength of concrete decreased with further increases of pozzolan, for example, 15% replacement.

The effect of adding slag pozzolan together with $FeNi_3$ nanoparticles on compressive and tensile strength of concrete. As the amount of pozzolan was increased, the compressive and tensile strength of the samples with 2% of $FeNi_3$ nanoparticles decreased.

The sample without pozzolan had the highest compressive strength of the samples with 2% of $FeNi_3$ nanoparticles. In the samples with 2% of $FeNi_3$ nanoparticles, which also contained pozzolan, the compressive and tensile strength decreased with the increase of the amount of pozzolan, so that the compressive strength of the samples with 10% and

Table 3: Details of the mixing plan for the control sample.

Specimen	Cement (kg/m^3)	Water (kg/m^3)	Pozzolan (kg/m^3)	$FeNi_3$ (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Superplasticizer (kg/m^3)
CP0F0	400	180	–	–	1,225	525	0.6
CP5F0	380	180	20	–	1,225	525	0.6
CP10F0	360	180	40	–	1,225	525	0.6
CP15F0	340	180	60	–	1,225	525	0.6
CP0F1	396	180	–	4	1,225	525	0.6
CP5F1	376	180	20	4	1,225	525	0.6
CP10F1	356	180	40	4	1,225	525	0.6
CP15F1	336	180	60	4	1,225	525	0.6
CP0F2	392	180	–	8	1,225	525	0.6
CP5F2	372	180	20	8	1,225	525	0.6
CP10F2	352	180	40	8	1,225	525	0.6
CP15F2	332	180	60	8	1,225	525	0.6
CP0F3	388	180	–	12	1,225	525	0.6
CP5F3	368	180	20	12	1,225	525	0.6
CP10F3	348	180	40	12	1,225	525	0.6
CP15F3	328	180	60	12	1,225	525	0.6

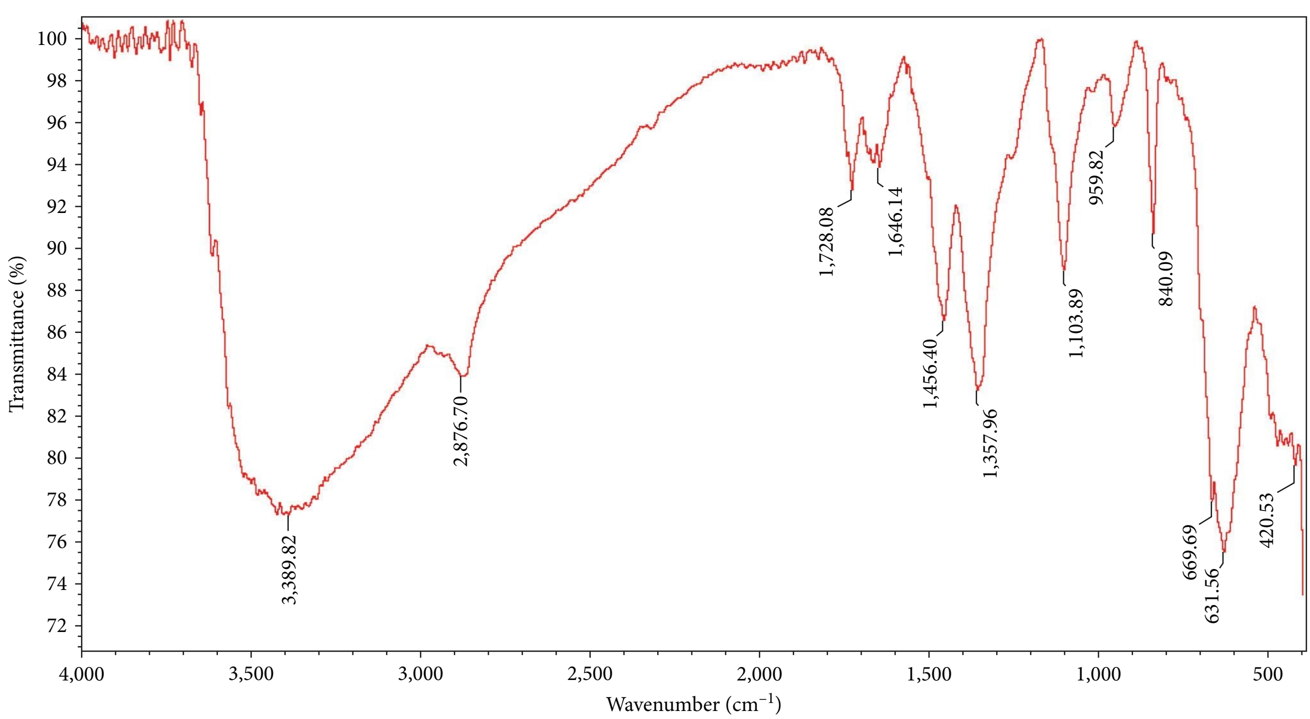


Figure 2: FTIR spectrum of $FeNi_3$.

15% of pozzolan was lower than the control samples. Although by increasing the amount of used pozzolan up to about 15% of cement weight, the compressive and tensile strength decreased compared to samples without pozzolan, but it is valuable for the reduction of cement consumption and consequently the reduction of environmental pollution.

The compressive and tensile strength of the samples containing 2% of $FeNi_3$ nanoparticles without pozzolan (27% and 18%) were higher than the control sample. By contrast, the samples containing 3% of $FeNi_3$ nanoparticles and 10% and 15% of pozzolan performed better than the control sample and showed lower compressive and tensile strength (Figures 8 and 9). The sample containing 2% of $FeNi_3$ nanoparticles had the highest compressive and tensile strengths.

3.2. The Effect of Adding Slag Pozzolan and $FeNi_3$ Nanoparticles on Water Absorption of Samples. Water absorption is one of the characteristics of concrete, which expresses the characteristics of its microstructure in terms of voids and their cohesion. Most of the destructive reactions that happen in concrete over time are

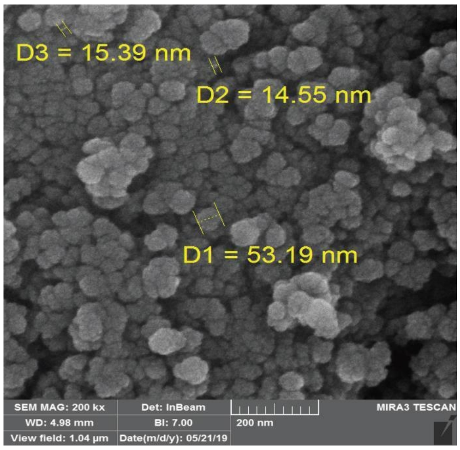


FIGURE 3: FESEM images of $FeNi_3$.

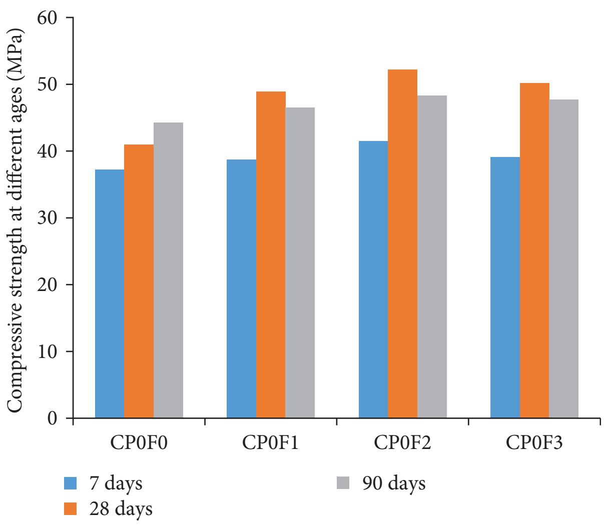


FIGURE 4: The effect of different amounts of $FeNi_3$ nanoparticles on the compressive strength at different ages.

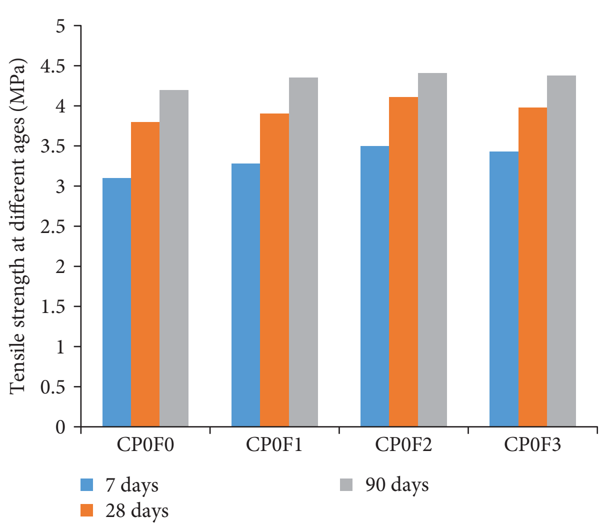


FIGURE 5: The effect of different amounts of $FeNi_3$ nanoparticles on the tensile strength of concrete.

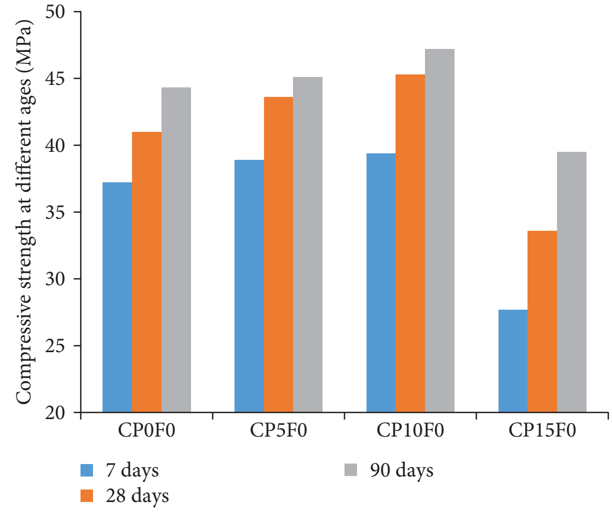


FIGURE 6: The effect of different amounts of pozzolan on the compressive strength of concrete.

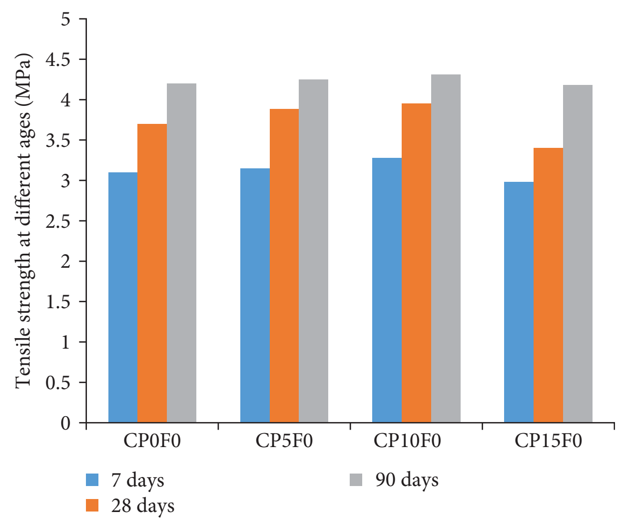


FIGURE 7: The effect of different amounts of pozzolan on the tensile strength of concrete.

due to the penetration of water, and water has always been a factor that initiates or accelerates destructive reactions in concrete. To absorb water, $10 \times 10 \times 10$ cubic concrete samples were placed in an oven at a temperature of 105 ± 5°C for 72 hr after curing for 28 days. After this time, the samples were removed from the oven and placed in clean water after cooling.

As shown in Figure 10, sample CP10F0 with 10% pozzolan had the lowest water absorption among samples without nanoparticles. Water absorption was lowest in sample CP10F2 with 10% of pozzolan and 2% of $FeNi_3$ nanoparticles. In the samples without pozzolan (CP0F2), the samples with 2% of $FeNi_3$ nanoparticles had the lowest water absorption (Figure 10). The addition of nanoparticles up to 2% reduces the water absorption of concrete, but an increase of 3% has a lesser effect on absorption.

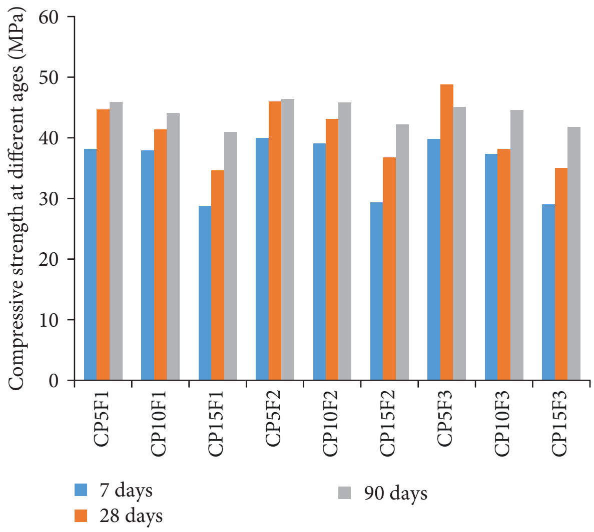


Figure 8: The effect of adding slag and $FeNi_3$ nanoparticles on compressive strength.

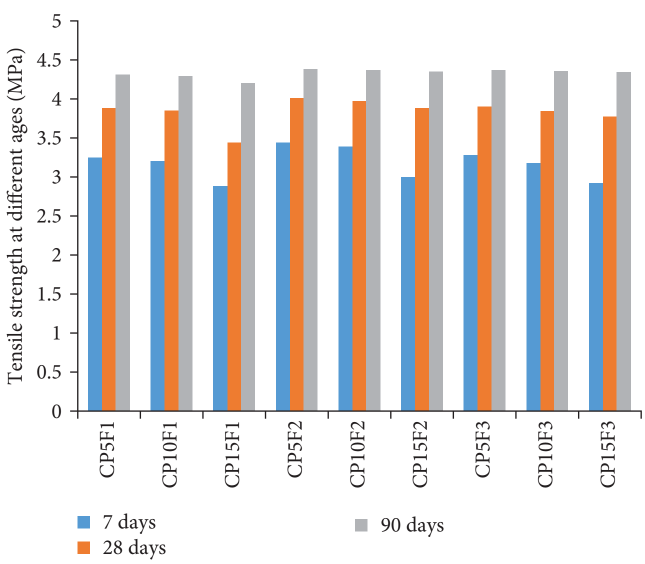


Figure 9: The effect of adding slag and $FeNi_3$ nanoparticles on tensile strength.

3.3. Scanning Electron Microscope Images of Concrete Samples.

Figure 11 shows SEM images of samples without nanoparticles and with 2% $FeNi_3$ nanoparticles. Adding FeNi3 nanoparticles to concrete improves its microstructure and reduces the internal voids of concrete (the surface of samples containing $FeNi_3$ nanoparticles is more uniform and dense), which makes concrete more durable. In addition, the increase of $Ca(OH)_2$ nanoparticles in concrete turns it into C–S–H gel (hydrated calcium silica), which reduces concrete pores and increases the strength and durability of concrete. In a similar alkaline environment in cement-based materials, the reaction between nanoparticles and $Ca(OH)_2$ is created. This reaction leads to the formation of a large amount of C–S–H gel. which reduces the pores and microcracks of the cement matrix. These results are consistent with studies [33].

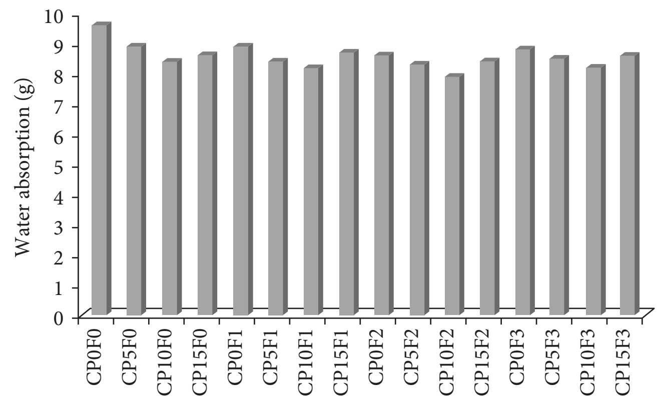


Figure 10: Effect of adding slag and nanoparticles on water absorption.

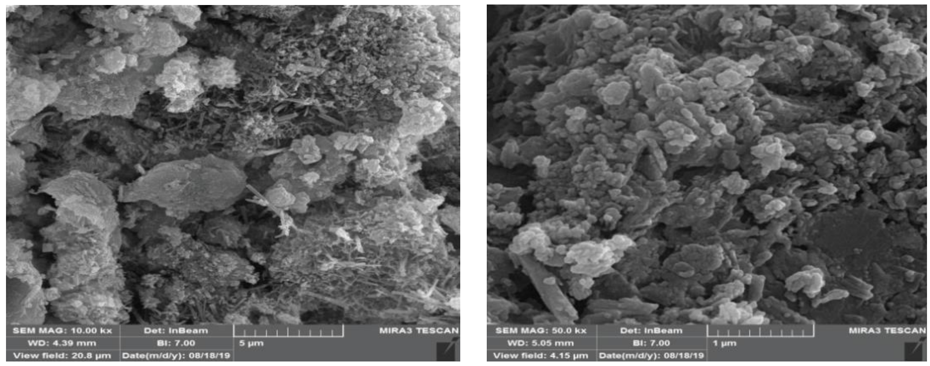
3.4. Effects of Adding Nanoparticles and Coal Slag on the Compressive Strength of Samples in 30% Sulfuric Acid Solution.

Compared to the control sample, samples containing 1% and 3% of $FeNi_3$ nanoparticles showed less change in compressive strength while placed in 30% sulfuric acid solution. Samples containing different percentages of nanoparticles will coal slag compressive strength compared to the control sample as shown in Figure 12. As a result of exposure to sulfuric acid, all samples showed a decrease in compressive strength. As the pozzolan was added to the samples, the compressive strength decreased. However, sample containing 10% pozzolan had higher compressive strength. Compared to other samples containing pozzolan. There for it is possible to reduce the negative environmental effects of cement consumption by substituting 10% cement weight by pozzolan.

Compressive strength of samples in 30% sulfuric acid solution with coal slag pozzolan and $FeNi_3$ nanoparticles. By substituting $FeNi_3$ nanoparticles for cement in Figure 12, slag pozzolan and slag pozzolan are in good harmony. Among samples with the same pozzolan, the compressive strength of samples containing 2% of $FeNi_3$ nanoparticles is higher compared to the other percentage of nanoparticles. Compressive strength decreased with increasing percentage of pozzolan in samples containing $FeNi_3$ nanoparticles.

3.5. Mass Reduction of Samples in 30% Sulfuric Acid by Adding Coal Slag Pozzolan and $FeNi_3$ Nanoparticles.

Based on the results of the tests, the CP0F2 sample containing 2% of $FeNi_3$ nanoparticles without slag had a lower mass loss in sulfuric acid solution. With the increase of slag, the effects of acid corrosion increased, and the concrete had a greater mass reduction than samples without slag. Samples CP0F1, CP0F2, and CP0F3 containing $FeNi_3$ nanoparticles without coal slag pozzolan had a lower mass reduction than the control sample (Figure 13). In samples CP5F1, CP10F1, CP15F1, CP5F2, CP10F2, CP15F2, CP5F3, CP10F3, and CP15F3, due to the presence of $FeNi_3$ nanoparticles, there was a lower mass reduction compared to samples CP5F0, CP10F0, and CP15F0. With the increase of $FeNi_3$, the effects of acid corrosion have decreased.



(a) (b)

FIGURE 11: Scanning electron microscope images. (a) Control sample and (b) sample containing 2% of nanoparticles.

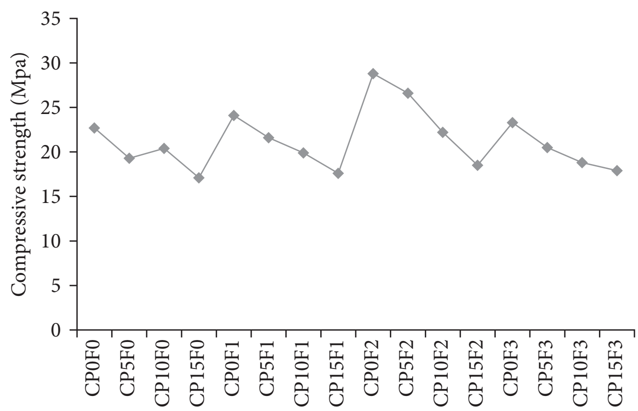


FIGURE 12: Effects of adding slag and $FeNi_3$ nanoparticles on the compressive strength of sulfuric acid solution.

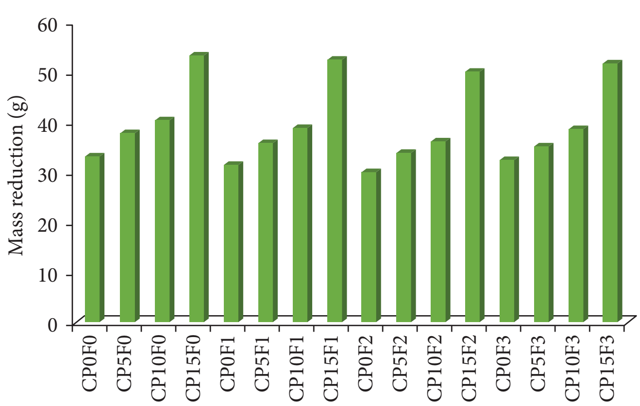


FIGURE 13: The effect of simultaneous addition of slag and $FeNi_3$ nanoparticles on reducing the mass of the samples.

3.6. Scanning Electron Microscope Images of Samples Exposed to Sulfuric Acid. Concrete is destroyed by sulfuric acid in two stages. In the first stage, sulfuric acid reacts with calcium hydroxide and hydrated calcium silicate to produce gypsum ($CaSO_4{\cdot}2H_2O$). Ettringite ($C_6AS_3H_{32}$) is formed when gypsum reacts with tricalcium aluminate (C_3A).

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 \cdot 2H_2O, \tag{1}$$

$$CaSO_4 \cdot 2H_2O + C_3A \longrightarrow C_6AS_3H_{32}. \tag{2}$$

Compared to the primary products, gypsum and ettringite occupy a larger volume, causing expansion and cracks in the concrete, which decreases its strength. Figure 14 shows the SEM of the control sample and the sample containing 2% of $FeNi_3$ nanoparticles. A crack in the concrete structure is caused by the formation of calcium sulfate crystals (plaster) in the form of board crystals. These pictures show that ettringite, which is more destructive than gypsum, is not formed in these concrete samples. These results are consistent with studies [34].

4. Conclusion

(1) In this study, $FeNi_3$ nanoparticles and coal slag were used as a partial of cement in concrete to investigate the mechanical properties and durability.

(2) SEM and FTIR spectra confirmed the accuracy of these nanoparticles synthesized in the laboratory. Due to their nanometer size and shape, the nanoparticles can penetrate the smallest pores and cavities in concrete.

(3) The compressive and tensile strength of 28-day concrete increased by 27% and 18%, respectively, when empty spaces were filled by nanoparticles.

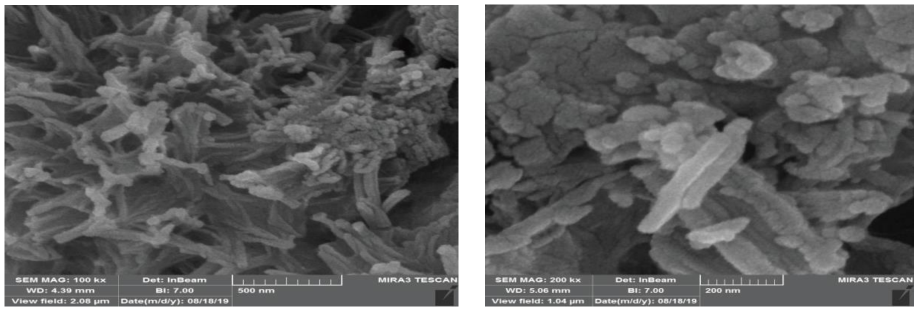
(4) Adding nanoparticles overs the disadvantage of vising pozzolan in concrete such as reduction of compressive and tensile stringiness.

(5) Calcium hydroxide decreased due to reaction with $FeNi_3$ nanoparticles. Resulting in the creating of more C–S–H (hydrated calcium silicate) gel, which improved the microstructure of concrete.

(6) In a sulfuric acid environment, coal slag pozzolan and nanoparticles increased the compressive strength of concrete.

(7) Adding coal slag up to 10% of cement weight. Slightly increased compressive strength of concrete.

(8) Coal slag reduced concrete's water absorption and improved its durability.



(a) (b)

FIGURE 14: Scanning electron microscope images. (a) Control sample and (b) sample containing 2% of $FeNi_3$ nanoparticles.

(9) Meanwhile, the use of coal slag in concrete is useful due to decreasing cement in concrete and consequently air pollution reduction.

(10) Considering the reduction of cement consumption and the positive effects of $FeNi_3$ nanoparticles in concrete, this study can create a new attitude in the industry.

Data Availability

The [DATA TYPE] data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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