Scientia Iranica A (2016) 23(6), 2557–2564

Sharif University of Technology
Scientia Iranica
Transactions A: Civil Engineering
www.scientiairanica.com

Research Note

Nanosilica effects on mechanical properties of concrete in crude oil products environment

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Received 3 October 2014; received in revised form 30 August 2015; accepted 21 November 2015

KEYWORDS
Nanosilica;
Petroleum products;
Sulfuric acid;
Compressive strength;
Bond strength;
Steel rebar.

Abstract. This investigation develops some important data on the mechanical properties, bond strength between concrete and steel rebar, and microstructure of crude oil-soaked Concrete containing silica fume and nanosilica. Experiments were performed in eight mixes with different percentages of nanosilica and different water-cement ratios. Concrete samples were cured in the petrol, gas-oil, 2.5% solution of sulfuric acid, and water. To conclude, considering the results, recommendations on optimization of nanosilica, silica fume, and water-cement ratio for this type of concrete for use in the construction of concrete tanks holding petroleum products are offered. The result shows that nanosilica can improve various properties of the concrete in corrosive conditions.

1. Introduction

Strength and durability of concrete structures in the petroleum industry, including oil storage tanks or pipeline networks of hydrocarbons, due to exposure by corrosive agents, have attracted much attention in the science of concrete technology. Recent research has shown that concrete destruction and corrosion in aggressive environments, such as marine environment and sanitation, are more prevalent compared with the other conditions. This phenomenon is due to the presence of various ions, such as sulfate, chloride, and magnesium, in this condition that cause destruction and severe corrosion in concrete. The first cause for worry is the concrete storage structures of hydrocarbons, which raise the possibility of damaging ions in these environments. Crude oil is an organic substance that is a combination of carbon and hydrogen. In addition, it contains impurities such as sulfur, nitrogen, and oxygen. Petroleum products, especially fuel products, such as petrol and kerosene, also contain some of these impurities. Researchers with different studies showed that sulfur-containing environments are damaging to cementitious materials and cause chemical destruction [1].

Results of the research conducted by Blaszczynski showed that oil products could reduce compressive strength around 10 to 50% over a period of 72 months [2].

Research by Hisham Diab showed that compressive strength of crude samples in oil in 280 days is slightly higher than the 28-day samples, the amount of which is almost 1.05 times higher. His results also showed that the resistance of the 280-day samples which was cured in the laboratory conditions is also higher than those samples that are processed into crude oil with the same cured age [3].

Ramezaniyanpour and Amiri showed that the strength of the 28-day specimens cured in oil has been

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Table 1. Components of the mix design.

Concrete type	Cement (kg/m^3)	Water (kg/m^3)	Water to cement	Modified cement (kg/m^3)	Silica fume (kg/m^3)	Nano silica (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Super plasticizer (kg/m^3)
HC	450	135	0.3	450	0	0	907.5	907.5	13.5
HS	450	135	0.3	405	45	0	907.5	907.5	13.5
HN-1.5	450	135	0.3	398.25	45	6.75	907.5	907.5	13.5
HN-3	450	135	0.3	391.5	45	13.5	907.5	907.5	14.5
LC	450	180	0.4	450	0	0	885	885	9
LS	450	180	0.4	405	45	0	885	885	9
LN-1.5	450	180	0.4	398.25	45	6.75	885	885	9
LN-3	450	180	0.4	391.5	45	13.5	885	885	10

reduced on average to about 15% of the crude samples in a laboratory environment [4].

Onabolu showed that the sample resistance decreased with increasing the amount of oil absorbed, but after 90 days, when oil absorption has reached a steady state, reduction of the resistance reaches a constant; he also showed that saturation specimens are not absorbed by oil. If there is an oil effect on specimens, the reaction is limited to the surface, and curing conditions have a significant role in strength characteristics and are absorbed in concrete [5].

Considering the effects of using nanosilica and silica fume in concrete, including improved microstructure, reduced permeability, and increased compressive strength [6-11], it can be argued that the use of nanosilica decreases absorption of oil by the concrete; furthermore, it has been shown that adding nanosilica to concrete improves durability against penetration of sulfate ions [12].

About bond strength of concrete and steel rebar, the results of previous studies showed that the corrosion of curing concrete in sulfuric acid caused decrease in bond strength of corrosion concrete and rebar [13]. Also, increasing the compressive strength will increase the bond strength of concrete and rebar steel [14-16].

In this study, the petroleum products are gas-oil and petrol, and investigation of the effect of the materials on properties of concrete seems necessary due to the presence of sulfur in these products. The effect of sulfuric acid on concrete properties was studied, and nanosilica was used to investigate the properties of concrete, exposed to aggressive conditions mentioned above.

2. Experimental program

In this study, to investigate the mechanical properties and durability of concrete specimens, 8 mix designs were considered with 180-day experimental program in accordance with Table 1 with a slump of 10.7 cm. To evaluate the bond strength of concrete and steel rebar, 48 samples were tested at the ages of 28 and 90 days of curing in water and soluble 2.5% sulfuric acid, and the results were compared. To study the microstructure of the concrete, X-Ray Diffraction (XRD) test was used. The number of test samples was 288 of which 72 samples of 8 mix designs were placed in water and the remaining samples in aggressive environments (gas-oil, petrol, a solution of 2.5% sulfuric acid) and tested at ages of 28, 90, and 180 days. The amounts of silica fume and nano silica were considered as cement replacement.

Samples were stored in aggressive environments. They were first cured for 7 days in the pool water, and then were measured and placed in an aggressive curing environment after a week of exposure in a laboratory environment.

3. Materials

Used nanosilica in this study is amorphous colloidal nanosilica soluble in water with concentration of 50%; specifications are shown in Table 2. Consumed silica fume has been prepared from Iran Ferro Alliyazh industry in Azna; its characteristics are presented in Table 3. Used fine aggregates (sand) are natural double washed out, and coarse aggregates (gravel) are broken mountain type. Portland cement used in this project

Table 2. Specifications of nanosilica.

Appearance	Density gr/cm^3	Weight percentage of SiO_2	PH	Viscosity	Average particle size	Percentage of silica in the solid phase	Specific surface m^2/g
White liquid	1.403	49-51.5	9.1	Max 15	34 nm	99.7%	70-100

Table 3. Specifications of silica fume.

SiO_2	Minimum specific surface (m^2/g)	Carbon percentage	Specific gravity (g/cm^3)
94.04%	20	0.5	2

is of type two and was bought from Delijan cement factory. Also, in this study, third generation super plasticizer based on dispersion melam,ine sulphonate is used to increase the workability M63. The used water in this project is the drinkable water of Arak.

Specifications of used gas-oil and petrol in this project have been provided by national petroleum products distribution company.

4. Mixture composition

To prepare the mix designs, first, the materials were weighed carefully. Then, weighed sand and gravel were initially poured into the electric tilt blender, and a homogeneous mixture of cement and silica fume was added to the mixture and mixing continued for 30 seconds. Then, half of the water mixes with half of the super plasticizer after stirring were added to the mixture and the mixture stirred for 1 minute. In the final stage, by the presence of nanosilica in the mix, half of the water with the remaining super plasticizer and nanosilica were mixed completely and added to the blender and mixing operations were performed for 2 minutes. Immediately after mixing ended, the slump test was carried out on the mixture. The molded samples were compacted by a shaking table. To prevent water evaporation from the surface of the molded concretes, the mold was covered with plastic covers and samples removed from the mold after 24 hours. Immediately after being removed from the molds, the samples were maintained in a pool of water with a temperature of about 19 to 23°C.

5. Testing methods

Concrete specimens were exited from the curing environment within the stipulated time and after cleaning off, water, oil, petrol, and sulfuric acid from the surface were examined after 24 hours according to relevant standards. Compressive strength test in accordance with BS 1881-88 and volumetric water absorption tests were performed according to standard BS 1881-122. For testing weight loss concrete, specimens exposed to solution sulfuric acid at specified intervals were removed from the acid and measured after brushing and cleaning of the surface. And, the bond strength testing of concrete and steel rebar was performed by 16 mm diameter, according to Rilem tensile standard on concrete samples as in Figure 1 by the rebar tension machine (Figure 2). X-ray diffraction experiment was taken at age of 90 days by Arak University's X-ray diffraction machine, Philips Xpert-pw3373 model with radiation Cu-$k\alpha$($\lambda = 1.54056$Å).

Figure 1. Bond testing of concrete and steel rebar samples. Mold dimensions: 15 × 15 × 15 cm.

Figure 2. Tensile testing machine for concrete and steel rebar.

6. Results and discussion

6.1. Compressive strength testing

Compressive strength test results at ages of 28, 90, and 180 days of curing aggressive environments are presented in Table 4.

Considering Table 4, it can be seen that the use of silica fume and nanosilica increases 28-day compressive strength of the concrete with water-cement ratio of 0.3 up to 20% and at the water-cement ratio of 0.4 up to 19.5%. Also, it was observed that the compressive strength of specimens with water-cement ratio of 0.3 was approximately 11% to 15% more than water-cement ratio of 0.4.

Table 4. Compressive strength of specimens at various ages and conditions.

Concrete mixtures	Compressive strength (MPa)											
	28-day				90-day				180-day			
	W[a]	$H_2SO_4^b$	P[c]	G[d]	W	H_2SO_4	P	G	W	H_2SO_4	P	G
HC	63.0	59.5	62.2	63.0	67.4	48.0	64.0	61.4	69.0	35.0	64.5	61.7
HS	75.5	72.3	74.5	73.1	80.1	62.5	76.3	71.3	80.9	48.3	76.3	68.5
HN-1.5	75.9	72.7	74.9	73.8	79.5	62.3	75.1	72.3	81.5	55.5	76.5	72.7
HN-3	76.8	74.8	75.7	75.5	80.1	63.5	76.8	75.1	82.0	54.0	77.5	76.3
LC	56.7	51.4	54.7	55.3	65.5	39.2	58.2	56.0	65.6	31.2	59.2	57.2
LS	64.3	60.6	61.7	62.1	74.7	51.2	67.1	63.5	75.1	37.7	68.6	64.1
LN-1.5	66.5	62.5	65.0	65.1	73.7	56.3	68.1	67.5	74.0	48.0	68.0	66.8
Ln-3	67.8	61.8	66.1	67.2	75.0	54.3	68.5	68.2	76.0	47.1	69.0	67.2

[a] W: Water; [b] H_2SO_4: Sulforic acid; [c] P: Petrol; and [d] G: Gas-oil.

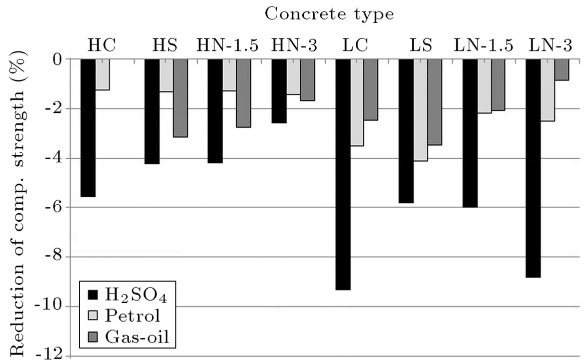

Figure 3. Reduction of 28-day compressive strength of concrete specimens compared with a cured condition in the water.

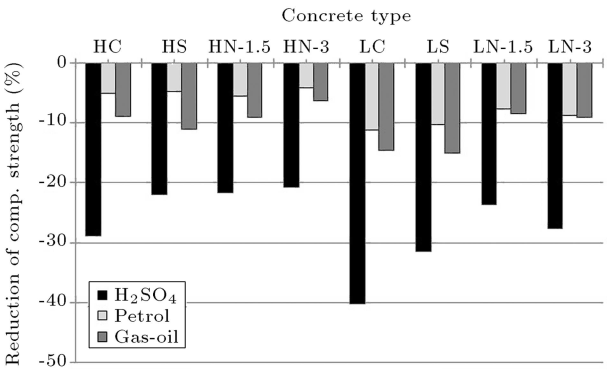

Figure 4. Reduction of 90-day compressive strength of concrete specimens compared with cured condition in water.

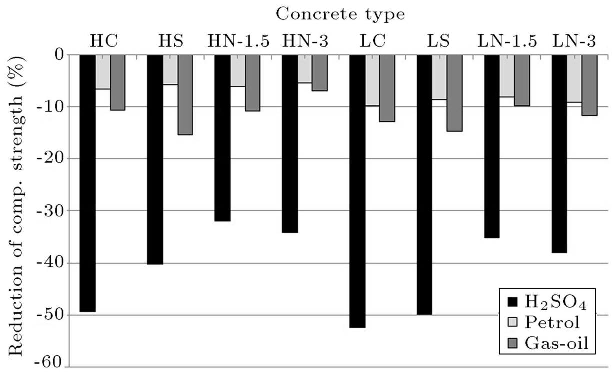

Figure 5. Reduction of 180-day compressive strength of concrete specimens compared with cured condition in water.

Also in Figures 3 to 5, the percentage of compressive strength reduction is shown under the effect of corrosive environments at the age of 28, 90, and 180 days compared to samples in water and at the same age.

According to the results in Figures 3 to 5, the greatest effect on the strength of the different ages is sulfuric acid solution of 2.5%. The most significant effect of sulfuric acid is observed at 28 until 180 days of the LC sample, about 52%. In this sample, silica fume and nanosilica were not used and the water-cement ratio is 0.4. The lowest amount of sulfuric acid effect is in 180 days on concrete samples of HN-3, HN-1.5, LN-1.5, and LN-3 that compressive strength reduction is 34, 31, 35, and 38%, respectively. At gas-oil curing condition, the most significant effect on reduction compressive strength is in 180 days on LC, LS, and HS samples with 12.8, 14.7, and 15.3%, respectively, compared with the cured sample at the same age. A minimum reduction of strength in 28 days is from HC sample with a water-cement ratio equal to 0.3. At age of 180 days, the lowest strength reduction was observed in the HN-3 sample. At all ages, decreased strength of the specimens with water-cement ratio of 0.4 is higher than that of the specimens with water-cement ratio of 0.3. In petrol curing condition, minimum reduction of strength is for sample HN-3 with 5.5%.

6.2. Bond strength test of concrete and steel rebar

Pulling out rebar stop happens at two different moments: 1- pulling out rebar without breaking concrete piece, and 2- pulling out rebar with breaking concrete piece.

Figure 6. Failure of concrete containing silica fume (HS) during the pulling out of steel rebar.

Figure 7. Exit steel rebar of LC specimen cured in a H_2SO_4 solution without fracturing concrete piece.

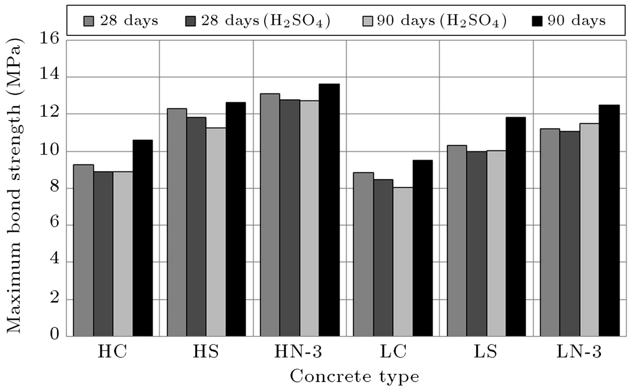

Figure 8. Variation of bond strength of concrete specimens.

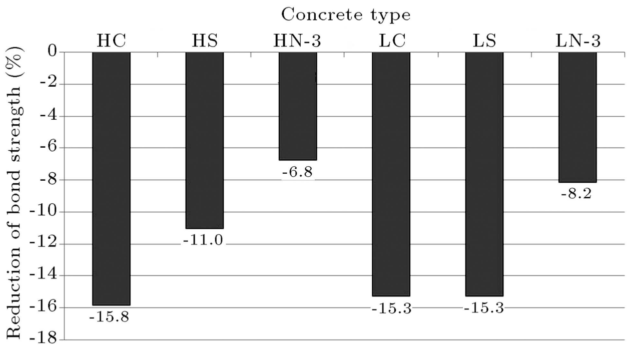

Figure 9. Reduction of bond strength of the samples cured in acid to the water condition at the age of 90 days.

Pulling out with the failure of concrete occurred in high strength concrete in samples that silica fume and nanosilica were used (Figure 6). In LC, with water-cement ratio of 0.4, pulling out happened with no fractures because of low compressive strength (Figure 7).

Bond strength test results at ages of 28 and 90 days of curing in water and sulfuric acid conditions are both shown in Table 5. It should be noted that the samples cured in sulfuric acid solution were first cured in water for 7 days and placed in acid after this period.

Figure 8 also shows the bond strength of different admixtures in both curing conditions.

In Figure 9, reductions of bond strength specimens cured in a solution of sulfuric acid are compared with the samples cured in water at age of 90 days.

Table 5. Maximum bond strength of concrete specimens at different ages and curing conditions.

Concrete mixtures	**Maximum bond strength (MPa)**			
	28-day	**28-day (H_2SO_4)**	**90-day**	**90-day (H_2SO_4)**
HC	9.3	8.9	10.6	8.9
HS	12.3	11.8	12.6	11.3
HN-3	13.1	12.8	13.7	12.7
LC	8.9	8.5	9.5	8.0
LS	10.3	10.0	11.8	10.0
LN-3	11.2	11.1	12.5	11.5

Considering Table 5 and Figure 8, it can be seen that the addition of silica fume and nanosilica increases the bond strength of concrete and rebar. The HN-3 sample shows a 40% increase in 28 days compared to the HC control sample. About the specimens with 0.4 water-cement ratio, for the 28-day sample, increasing the bond strength of LN-3 sample is 37% of the LC sample. This increase can be further improved and compressed by creating C-S-H in cement paste. The addition of Nano silica and silica fume caused the Interfacial Transition Zone (ITZ) in concrete to improve; thus, in contact with the cement paste with aggregates, was created greater compression and strength, which prevents the segregation of cement paste and aggregates during slip rebar. Figure 9 also shows that the lowest strength reduction, due to the sulfuric acid attack of concrete and rebar, occurs in specimens with silica fume and Nano silica. This happens due to the addition of silica fume and Nano silica by reduction of permeability of concrete and causes the corrosion of steel and concrete to reduce. In Figure 10, the relationship between compressive strength and bond strength of concrete and rebar has been shown.

Observing Figure 10 shows that by increasing

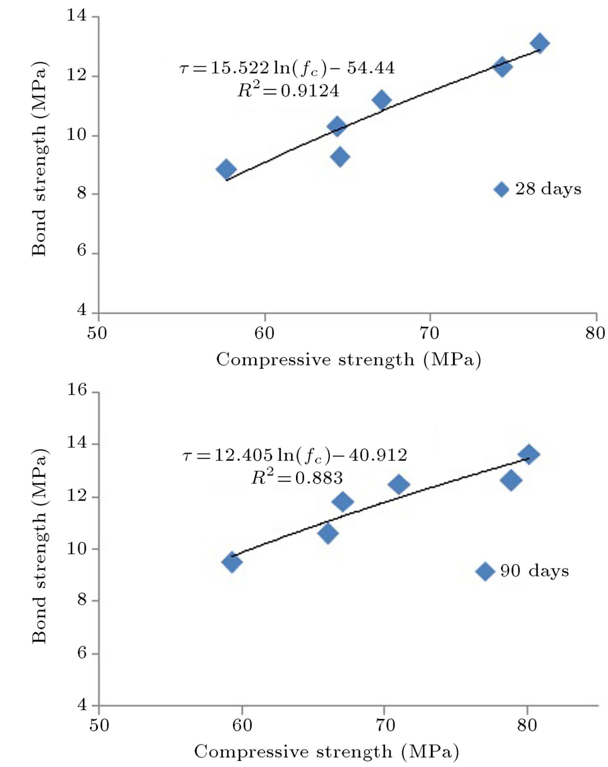

Figure 10. Relationship between compressive strength and bond strength of concrete and rebar.

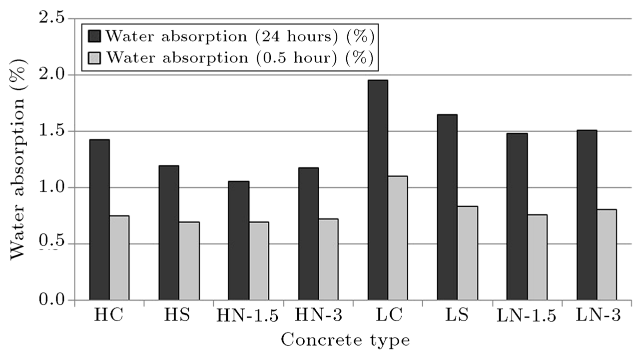

Figure 11. Percentage of water absorption of concrete specimens.

compressive strength, bond strength of concrete and steel rebar increases.

6.3. Volumetric concrete absorption experiments

To perform this experiment, three 10×10 cubic samples per mix design were used, and results of water absorption were obtained from 3 samples. Figure 11 shows the results of water absorption.

Adding silica fume and nanosilica reduces water absorption of concrete. HS, HN-1.5, and HN-3 admixtures in water-cement ratio of 0.3 have a little water absorption. So, a reduction of 24-hour water absorption in these samples, compared to HC control samples, is 17, 26, and 17%, respectively.

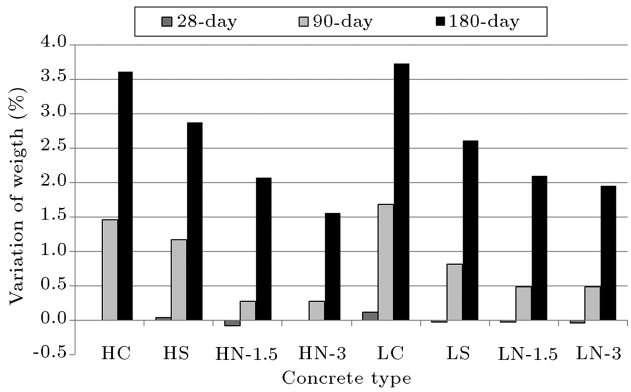

Figure 12. Percentage of concrete weight loss of specimens exposed to acid.

6.4. The test of concrete weight loss exposed to sulfuric acid solution

The obtained results of concrete weight loss in the acid for the supposed samples for ages of 28, 90, and 180 days are presented in Figure 12.

According to Figure 12, it can be seen that for the water-cement ratio of 0.4, the corrosion rate of the specimens is more than water-cement ratio of 0.3. With replacement of 3% nanosilica and 10% silica fume, the corrosion rate is less than 2 times the sample with the similar water-cement ratio; it shows the significant effect of silica fume and nanosilica on increasing the durability of concrete.

6.5. XRD testing results

In Figure 13(a) to (f), the X-ray spectrum of different concrete specimens in water-cement ratio of 0.3 and 0.4 is shown.

Figure 13 shows the variation of interaction between $Ca(OH)_2$ and nanosilica or silica fume at the interface with time determined by XRD pattern. The consumption of $Ca(OH)_2$ (crystals) content at the interface between glass plate and paste containing nanosilica or silica fume can be demonstrated approximately by intensity changes of main diffraction peaks of $Ca(OH)_2$ crystals.

Considering Figure 13, the maximum peak of crystalline $Ca(OH)_2$ was obtained at $2\theta°$ angles of 21 and 39°. Peak intensity in Figure 13 indicates that both nanosilica and silica fume have been effective in reducing the rate of calcium hydroxide in cement paste. For example, the peak intensity $2\theta°$ angle of 39 degrees in the HC sample is 64 counts. That, for this amount, HS and HN-3 samples are reduced to 44 and 25 counts, respectively. In the LC sample, the amount of calcium hydroxide peak at $2\theta°$ angle of 39° is 59 counts, which were obtained as 42 and 25 counts in the LS and LN-3 samples, respectively.

The results indicate that nanosilica can consume more $Ca(OH)_2$ crystals at the interface and can improve the interface structure more effectively than silica

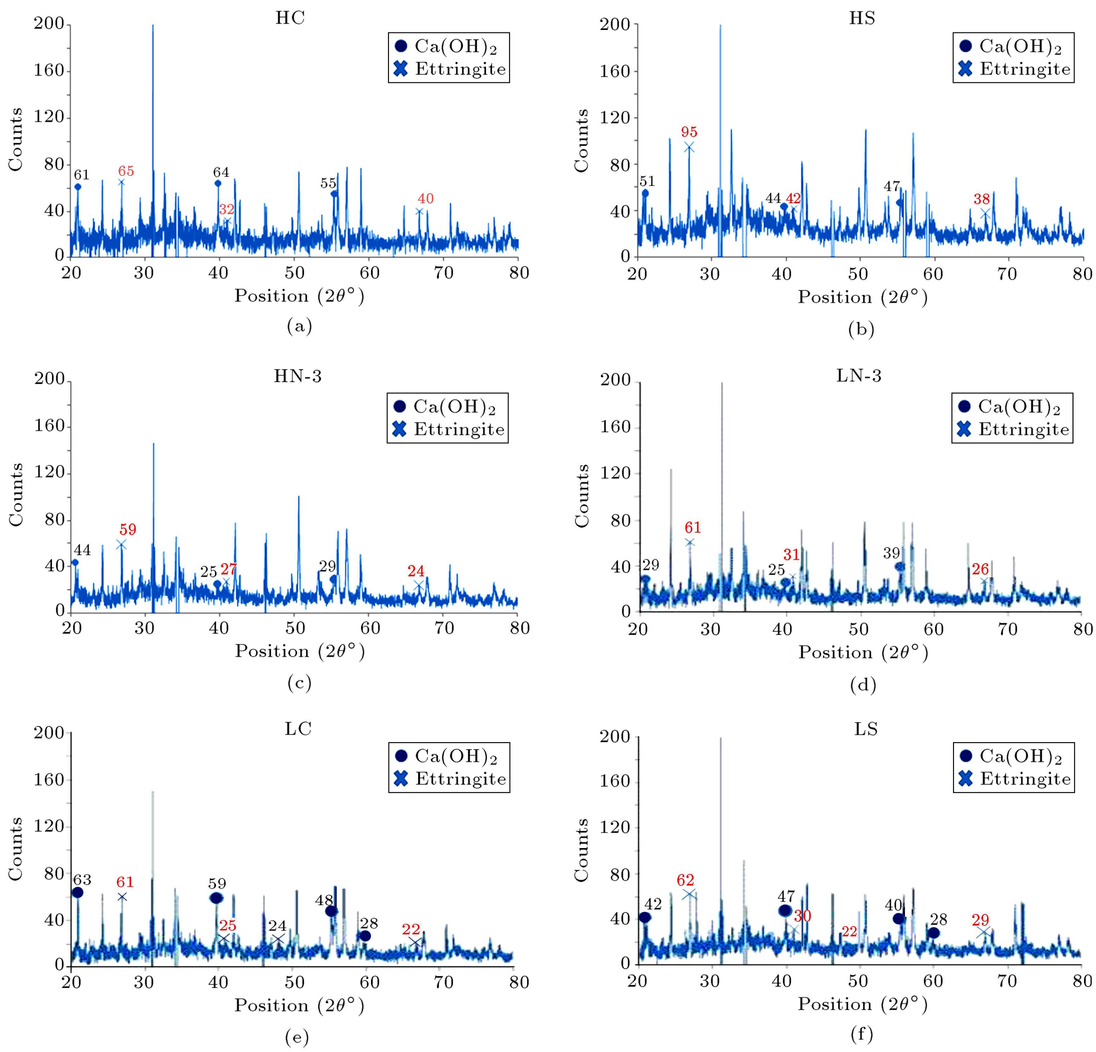

Figure 13. XRD spectrums of concrete samples.

fume, and also the pozzolanic activity of nano SiO_2 is much greater than that of silica fume. Nano SiO_2 consumes $Ca(OH)_2$ crystals, decreases the orientation of $Ca(OH)_2$ crystals, reduces the size of $Ca(OH)_2$ crystals at the interface, and improves the interface structure more effectively than silica fume.

7. Conclusion

Based on studies, conducted experiments, and discussions, the following results are noteworthy:

1. Petroleum products in the long time period caused concrete strength to reduce; the reduction in the strength of concrete specimens exposed to gas-oil is more than concrete specimens exposed to petrol;
2. Using nanosilica and silica fume increases concrete strength against the damaging effects of petroleum products and causes less reduction of the concrete strength of sulfate ions attack;
3. The best admixture contains 10% silica fume and 3% nanosilica. Compressive strength obtained 802 kg/cm^2 at the age of 180-day, which shows a 20% increase of the controls mix design strength;
4. Adding nanosilica and silica fume increased the bond of concrete and steel rebar, which is why it can improve the Interfacial Transition Zone (ITZ) of concrete;
5. Increasing compressive strength increases bonding of concrete and steel rebar;
6. Adding nanosilica and silica fume causes water absorption to reduce. Admixture containing 10% silica fume and 1.5% nanosilica is the best mix in terms of reduction permeability;
7. Existing nanosilica and silica cause crystals of calcium hydroxide to reduce in the concrete and production of dense C-S-H gel, and improve the microstructure of concrete, thereby reducing the corrosion of sulfate reaction, calcium hydroxide, and produced gypsum;

8. Finally, based on obtained results so far, it can be concluded that employing HN-3 mixture with 3% nanosilica is recommended for concrete storage tanks of petroleum products. Actually, for an economical usage of the supposed design, employing HN-1.5 mixture with 1.5% nanosilica can be replaced.

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