Effect of Corrosion Inhibitor Admixtures on Properties of Fresh and Hardened Concrete

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ABSTRACT—The corrosion of the reinforcement concrete structures is a significant problem for concrete infrastructures which leads to forming expansion, loss of bond between rebars and concrete, loss of effective area of rebar, cracking, and eventual spalling of the concrete cover. Finally, the corrosion may cause structural damage to concrete structures. The corrosion inhibitor admixture is one of the different techniques used to protect the steel reinforcement. In this research, the effect of adding different corrosion inhibitor admixtures on the properties of fresh and hardened concrete was investigated experimentally. Three different inhibitors were added individually in a concrete mix by a certain dosage which is a percentage from concrete volume. The inhibitors were amino and ester-based inhibitor, nitrite-based inhibitor, and phosphate-based inhibitor. Workability, compressive strength, tensile splitting strength, bond strength, and microstructure of concrete were evaluated. The obtained results are compared with findings reported in the literature. The findings of this research recommend the best of the examined inhibitors depending on the one that has the least negative effect on concrete properties. The best inhibitor of the studied three inhibitors is the nitrite-based inhibitor, which exhibited good compressive strength improvement in the acidic medium. Under scanning electron microscopy, the nitrite-based inhibitor exhibited more compact structure than other mixes.

Index Terms— Concrete, Corrosion, Corrosion inhibitors, Workability, Compressive strength, Tensile splitting strength, Bond strength.

1 Introduction

The Corrosion of steel reinforcement in concrete structures is becoming a significant structural and financial problem as it affects the service life of the concrete structures. Due to carbonation and/or chloride penetration, the passive layer around the reinforcing steel is destroyed, leaving the steel bar unprotected to the effect of corrosion. So, it is very important to try to inhibit corrosion as possible without affecting concrete properties. Various techniques have been developed with the intent of preventing the corrosion and to enhance the service life. The techniques include the coating to the concrete surface, the coating to the reinforcement, cathodic protection, alternative reinforcement, and corrosion inhibitors admixtures. Among all the available techniques, the use of corrosion inhibitors admixtures is one of the most appropriate and efficient methods for corrosion protection of reinforced concrete structures due to the easy operation, low cost, and excellent corrosion resistance effect.

As per NACE international, "A corrosion inhibitor is a substance when added to an environment, either continuously or intermittently to prevent corrosion by forming a passive film on the metal" [1].

An ideal corrosion inhibitor could be the chemical compound which when added to concrete can inhibit corrosion of embedded steel and has no adverse effect on the properties of concrete. Several commercial corrosion inhibitors are marked for use in reinforced concrete. There are basically three groups of inhibitors: anodic, cathodic, and mixed inhibitors [2]. Anodic inhibitors form an insoluble protective film on anodic surfaces to passivate the steel. Cathodic inhibitors form an insoluble film on the cathodic surface of the steel. Mixed inhibitors influence both the anodic and cathodic reaction sites by forming an adsorptive film on the surface of the metal.

Studies on chemical inhibitors concentrating on the efficiency of the inhibitor as a corrosion resistance compound only, most of the studies reported were on the efficiency of the inhibitor as a chemical substance when added to the concrete will inhibit or prolong the time to initiation of corrosion despite its effect on mechanical properties of concrete. The most commonly studied inhibitor for concrete is the nitrite-based for the aim of corrosion resistance [1–6]. Also, the nitrate-based inhibitor was studied to inhibit the corrosion but it does not have a good effect as a nitrite-based inhibitor [3]. Some studies discussed the effect of using phosphate as a corrosion inhibitor [1,7,8]. Other studies discussed the effect of organic inhibitor in the corrosion inhibition process especially [1,2,9]. Few studies are available discussing some concrete mechanical properties, and they used different inhibitors from that in our research.

J.J.Shi et al. [7] studied the effect of sodium nitrite and sodium phosphate on flexural strength and compressive strength at 28 days and long-term exposure to the atmospheric environment (360 days). The results showed that the mortar specimens with phosphate relatively increased setting time and lower early mechanical properties. Also, results showed that phosphate has little effect on the long-term mechanical properties of mortars. Sodium phosphate had the lowest flexural and compressive strength compared to sodium nitrite and blank specimens at

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early and long-term stages. De Schutter et al. [10] studied the effect of calcium nitrite-based inhibitor, amino, and ester-based organic inhibitor, amino alcohol-based inhibitor, and a migrating corrosion inhibitor on some concrete properties. The results showed that calcium nitrite-based inhibitor increases the early age compressive strength, the ultimate compressive strength seems to depend on the amount of inhibitor, increases somewhat the air content as well as the workability. An amino and ester-based organic inhibitor causes a decrease of compressive strength by about 10-20%, workability is not clear and the air content might be slightly increased. An amino alcohol-based inhibitor seems to decrease the compressive strength, while the workability tends to be increased and the air content might be slightly increased. A migrating corrosion inhibitor decreases the early age concrete strength while the ultimate compressive strength seems to be improved, workability might depend on the way in which the inhibitor is added and the air content might be slightly increased.

J.O. Okeniyi et al. [11] studied the effect of potassium-chromate and sodium nitrite on compressive strength. Results showed that concrete admixed with 0.145M potassium-chromate exhibited optimum inhibition effectiveness with good compressive strength in the acidic medium. In the saline medium, the concrete admixed with 0.679M sodium-nitrite exhibited optimal inhibition performance, but with reduction in concrete compressive strength. Zunyun Li et al. [12] studied the effectiveness of amino alcohol-based corrosion inhibitor and its influence on compressive strength. The results showed that amino alcohol-based corrosion inhibitor decreases somewhat the early age concrete strength, while the ultimate compressive strength seems to be improved. Al Zubaidy et al. [13] studied the effect of three commercial inhibitors which are calcium nitrite inhibitor, anodic corrosion inhibitor, and RHEOCRETE 222+ (combination of amines and esters) on reduction of corrosion process and on compressive strength. The results showed that calcium nitrite has the lowest 14 days compressive strength and the highest 28 days strength.

Accordingly, further studies are required for evaluating the properties of concrete containing the inhibitor. The experimental work in this paper is part of an extended study for the effect of adding different corrosion inhibitors on the properties of fresh and hardened concrete and the efficiency of protection for different corrosion inhibitors in the aggressive environment. The target of this research is to investigate the effect of adding different corrosion inhibitors on the properties of fresh and hardened concrete with certain dosages.

2 METHODOLOGY

The present research consists of a comparative experimental study of addition of corrosion inhibitors on the properties of fresh and hardened concrete. The workability, compressive strength, tensile splitting strength, bond strength, and micro-structure of concrete were evaluated. Three inhibitors were used in this research, two commercials, and one was prepared in the lab. The two commercials were amino and ester-based inhibitor (AI), nitrite-based inhibitor (NI), and the third which was prepared in the lab was phosphate-based inhibitor (PI) Four concrete mixtures with target compressive strengths of 30 MPa were prepared, which consisted of one control mix (C) without inhibitor and three mixes using the three types of inhibitors.

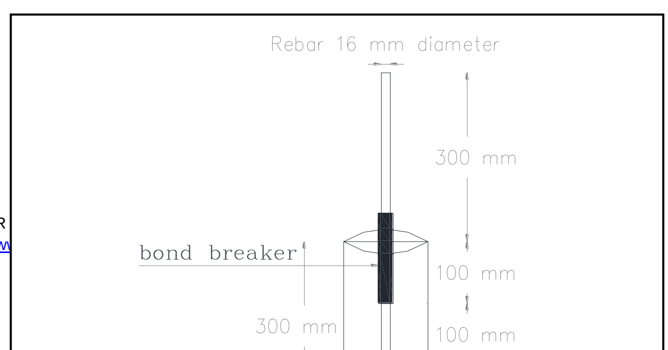
3 EXPERIMENTAL PROCEDURE

An overall of four series of mixtures were prepared in the laboratory. The control/blank mixture (C) was composed of cement, fine aggregate, coarse aggregate, water, and superplasticizer. The other three concrete mixtures that had inhibitors had been made by the same mixture of the control mixture in addition to mixing each inhibitor individually in each separate mix. The ratios of used inhibitors were 1.3% for AI as recommended in the datasheet of the commercial product, 3% for NI as recommended in the datasheet of the commercial product, and 3% for PI of the weight of cement. The superplasticizer was used with a ratio of 1.25% by weight of cement. For all mixtures, 0.45 w/c was used. Table 1 shows the constituents of each mix.

TABLE 1: MIXTURES CONSTITUENTS PER ONE CUBIC METER OF CONCRETE (KG).

Mix ID	Cement content	Aggregate		Water content	Inhibitor content	Super plasticizer
		Fine	Coarse			
C	375	700	1050	180	0.00	4.70
AI	375	700	1050	180	5.00	4.70
NI	375	700	1050	180	12.00	4.70
PI	375	700	1050	180	12.00	4.70

A slump test was conducted to evaluate the workability of mixes. 24 Cubes of 150 mm x150 mm x150 mm were cast for compressive strength test, the strength was determined at 7 and 28 days [14]. The tensile splitting strength was performed at 28 days on 12 cylinders of 100 mm diameter and 200 mm height [14]. The pullout test was performed at 28 days on 12 cylinders of 150 mm diameter and 300 mm height using a rebar of 16 mm diameter. Also by using a bond breaker, the same criteria of ASTM D 7913/D 7913M [15] as shown in Fig.1. The bond breaker was a plastic hollow tube of 18 mm diameter and 150 mm height that was installed in the first 100 mm of the bar length that embedded in the concrete cylinder. The purpose of using a bond beaker was to ensure that the failure will occur because of the bond between steel bar and concrete.



3.1 Materials

The cement used was Portland cement of grade R42.5 that complies with the requirement of the Egyptian standard specifications (ESS 4756/2007) [16]. The coarse aggregate was crushed limestone. Natural sand was used with fineness modulus of 2.40. The concrete mix was designed to achieve cube compressive strength after 28 days of 30 MPa. The steel reinforcement used was high tensile steel with oblique ribs of grade B500DWR. The steel nominal diameter was 16 mm for the pullout test. Three inhibitors are used in this research , two were commercials and one was prepared in the lab. The two commercials were identified as amino and ester-based inhibitor (AI), nitrite-based inhibitor (NI). Table 2 shows the properties of these inhibitors as stated in the manufacturer's product data-sheet. The third which was prepared in the lab was di-sodium hydrogen orthophosphate inhibitor (PI).

TABLE 2: PROPERTIES OF COMMERCIAL CORROSION INHIBITORS.

Property	Amino and ester-based inhibitor (AI) "MasterLife CI 222"	Nitrite-based inhibitor (NI). "Sika Ferrogard-901"
Density (Kg/l)	---------	1.06
PH value	---------	9-11
Recommended dosage	5 litre/m3 concrete	12 g/m3 concrete

3.2 Casting and curing of specimens

All mixes were batched in a tilting pan type mixer, as shown in Fig.2. A thin layer of mineral oil was used to coat the internal surfaces of the molds before pouring directly. Fresh concrete was poured into the molds and compacted using a vibrating table as shown in Fig.3. All the concrete specimens were demolded after 24 hours and then cured by submerged in a curing tank reaching the age of test at 7 and 28 days.

Fig.2. Tilting pan type mixer. Fig.3. After pouring directly.

4 RESULTS AND DISCUSSION

The overall test results for the specimens (slump test, compressive strength test, tensile splitting strength test, and bond strength test) were given in Table 3.

TABLE 3: THE TEST RESULTS FOR ALL MIXES.

Mix ID	Slump (mm)	Mean compressive strength * (MPa)		Tensile splitting strength * (MPa)	Bond Strength * (MPa)
		7days	28 days		
C	230	33.78	35.65	2.36	24.06
AI	270	30.28	30.84	1.91	23.04
NI	200	32.08	37.52	2.12	23.74
PI	140	26.97	28.57	2.09	16.74

* Mean strength was determined as the arithmetical mean of 3 specimens.

4.1 Workability

Fig.4 and 5 represent the effect of adding corrosion inhibitors on slump values for all mixes. The value of the C mix was taken as a reference value (i.e. 100%).

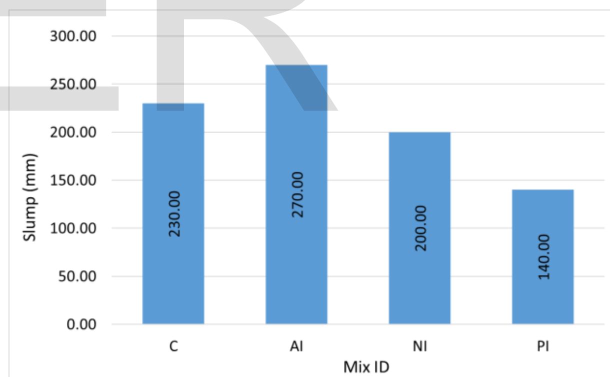


Fig.4. Slump values for C, AI, NI, and PI mixes

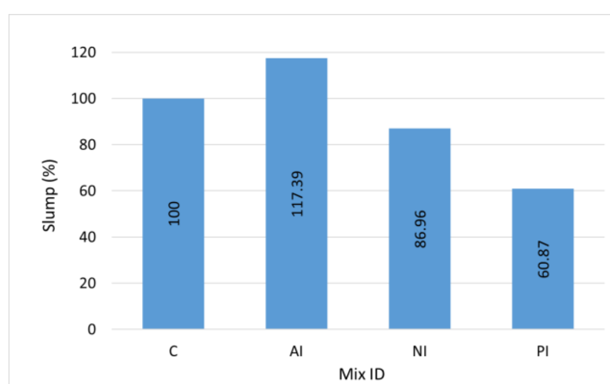


Fig.5. Percentage of slump values for all mixes.

Based on these values, the following points were observed:

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The C mix gets a slump value of 230 mm. The AI mix achieved a slump with 270 mm which indicates an increase on workability with 17.39% compared to C mix. The NI mix achieved a slump with 200 mm which indicates a decrease on workability with 13.04%, but within the range (+ or – 30 mm) as indicated in the Egyptian codes [14]. The PI mix achieved a slump with 140 mm which indicates a big decrease on workability with 39.13%.

Slump test results show that all mixes had different influences on workability with slump values different from each other and compared to the control/blank mix (C). Also, Nitrite-based inhibitor (NI) has the least effect on workability of the fresh concrete among all mixes containing inhibitors.

4.2 Compressive strength

Fig.6 and 7 represent the effect of adding corrosion inhibitors on the mean compressive strength, for all specimens at the ages of 7 and 28 days. The values of C mix were taken as a reference value (i.e. 100%). The percentage of mean compressive strength of AI, NI, and PI mix were compared to those of C mix.

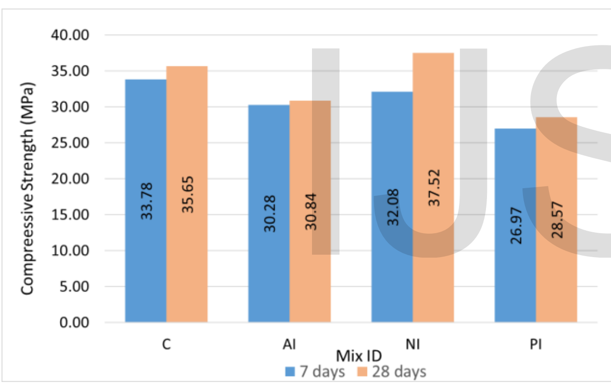


Fig.6. Mean compressive strength at 7 and 28 days for all mixes

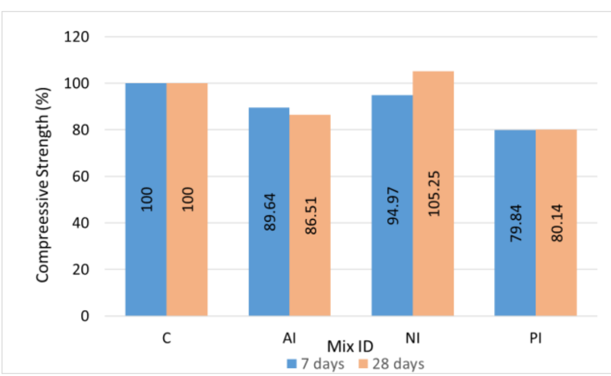


Fig.7. Percentage of mean compressive strength for all mixes.

Based on these values, the following points were observed:

A loss in the early age compressive strength was noticed in the AI, NI, and PI mixes by 10.36%, 5.03%, and 20.16% respectively. The late compressive strength decreased in AI and PI mixes by 13.49% and 19.86% respectively. While the late compressive strength of NI mix increased by 5.25%.

Several reasons might be the cause of the early age reduction in compressive strength as reported by many authors. One of the possible reasons is due to the retarding effect of these inhibitors [12]. The results of the compressive strength of the AI mix might be due to the slight increase in air content which is consistent with De Schutter et al. [10]. The effect of NI on the ultimate strength of concrete was different. Some research studies indicated a reduction in the ultimate strength by the use of NI as an admixture [11]. Also, some other studies show an increasing effect for NI on the ultimate strength [7]. The results in the present paper show an increase in the ultimate compressive strength of NI. This increase may be due to that some inhibitors react with concrete forming the complex thus reducing the permeability of the concrete [1].

4.3 Tensile splitting strength

Fig.8 and 9 represent the effect of adding corrosion inhibitors on the mean tensile splitting strength, for all specimens at the ages of 28 days. The values of C mix were taken as a reference value (i.e. 100%). The percentage of mean tensile splitting strength of AI, NI, and PI mix were compared to those of C mix.

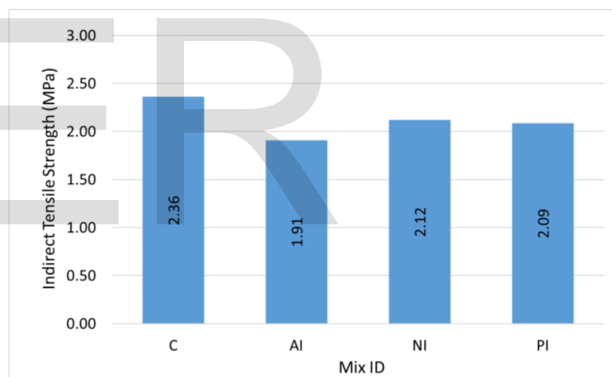


Fig.8. Mean tensile splitting strength at 28 days.

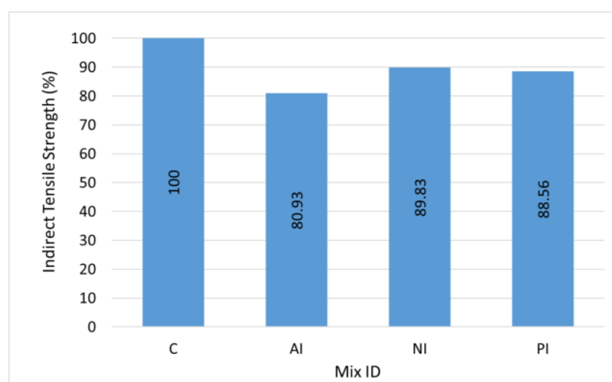


Fig.9. Percentage of mean tensile splitting strength for all mixes.

Based on these values, a reduction in tensile splitting strength occurs to all inhibitor mixes. The tensile strength decreased for AI, NI, and PI mixes by 19.07%, 10.17%, and 11.44%

respectively. A similar trend to that of compressive strength is noticed except that of NI mix.

4.4 Bond strength

Fig.10 and 11 represent the effect of adding corrosion inhibitors on the mean bond strength, for all specimens at the ages of 28 days. The values of C mix were taken as a reference value (i.e. 100%). The percentage of mean bond strength of AI, NI, and PI mix were compared to those of C mix.

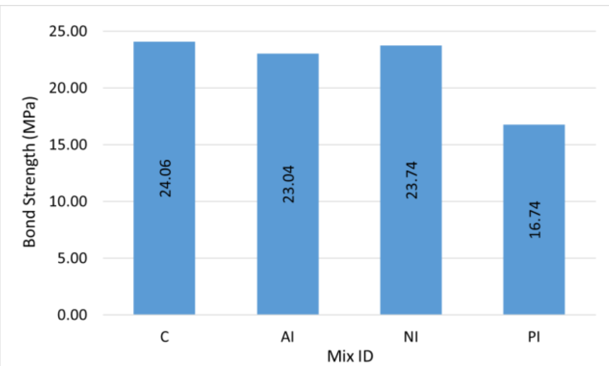


Fig.10. Mean bond strength at 28 days.

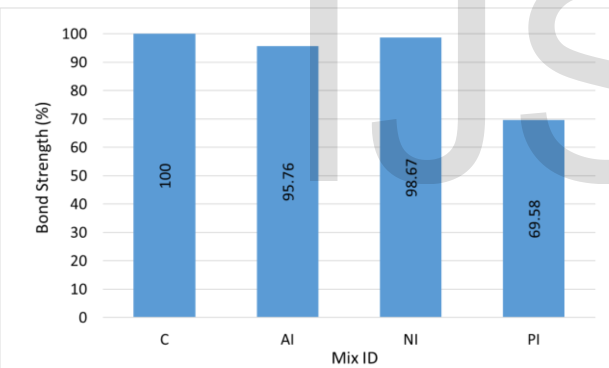


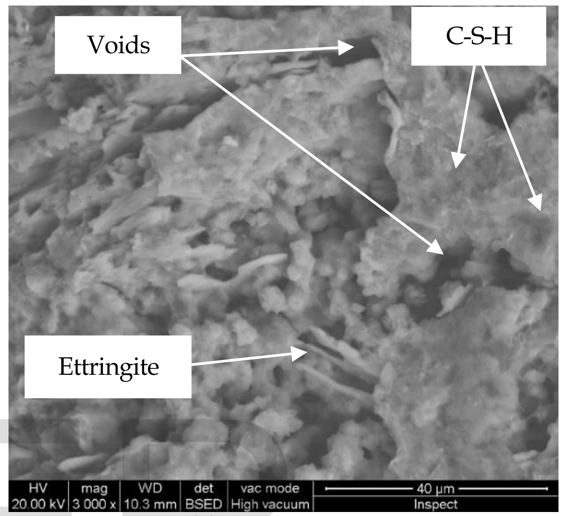
Fig.11. Percentage of Mean bond strength for all mixes.

Based on these values, the results of bond strength between the steel bar and concrete was affected by the addition of inhibitors. The bond strength decreased with 4.24%, 1.33%, and 30.42% for AI, NI, and, PI mixes respectively. This indicates that Nitrite-based inhibitor (NI) has a slight effect on the bond strength.

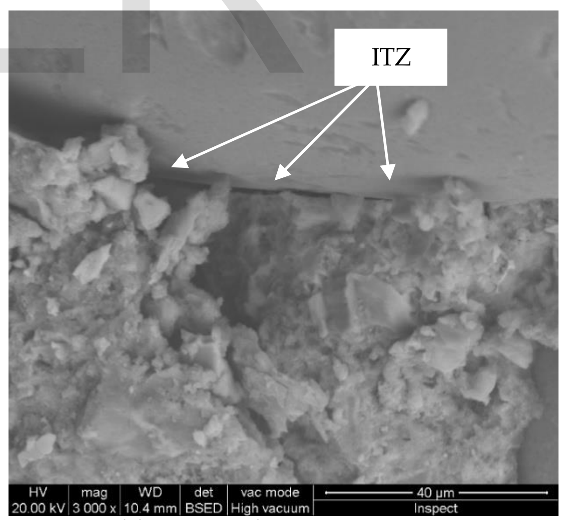
4.5 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) images were taken to study the microstructure for the materials of four specimens of three inhibitors showing the effect of inhibitors presence relative to the control mix without inhibitor.

Fig.12 show the SEM micrographs for the C mix which represent the ordinary structure of a mix. It can be observed that many loose fibrous C-S-H gels and crystalline ettringite needles are formed in the controlled/blank mortar. Fig.13 shows SEM micrographs with the presence of AI, the mortar contains a huge number of unfamiliar substances which indicate the inhibitor. The gap at the interfacial transition zone (ITZ) is not continuous around the coarse aggregate. Fig.14 shows SEM micrographs with the presence of NI, the mortar contains more compact C-S-H gels compared to blank mortar. The gap at ITZ is semi-closed around the coarse aggregate. Fig.15 shows SEM micrographs with the presence of PI, the mortar contains some micro cracks and voids. The gap at the ITZ was wide and continuous around the coarse aggregate.

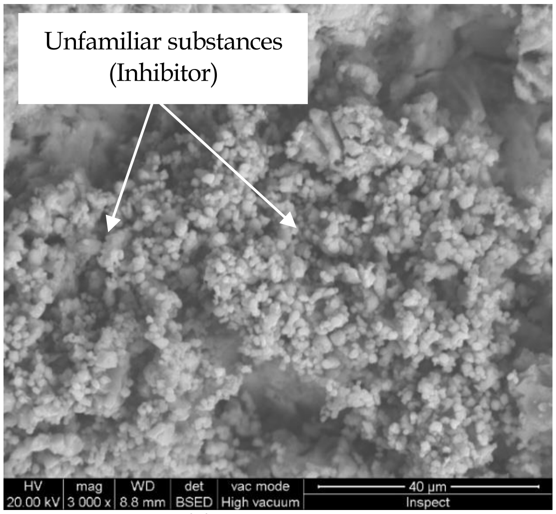


(a) At cement paste

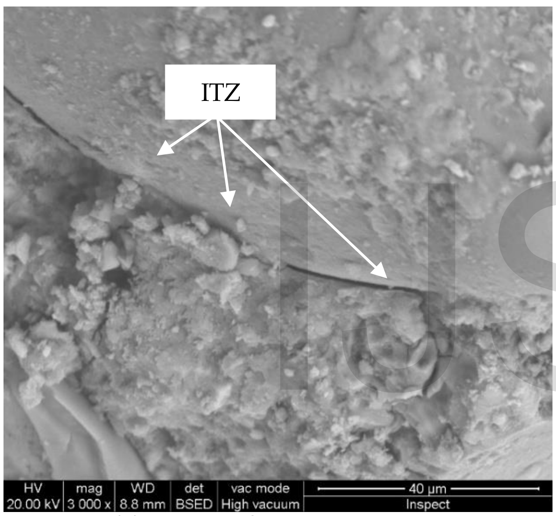


(b) At the interfacial transition zone

Fig.12. SEM micrograph of C mix for two different spots (a and b).

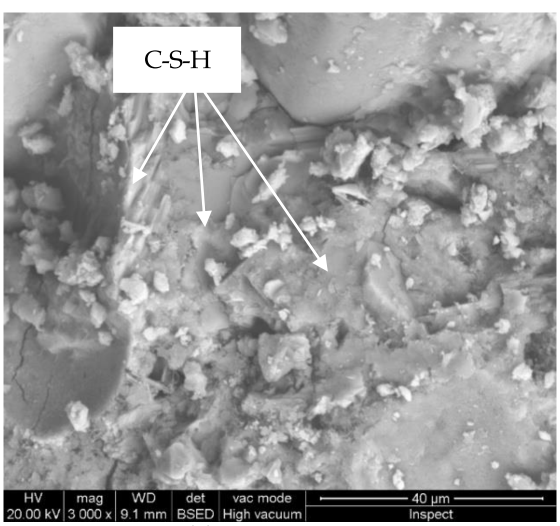


(a) At cement paste

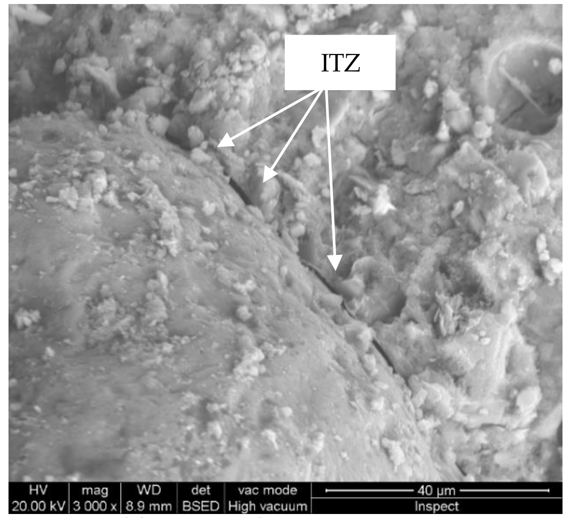


(b) At the interfacial transition zone

Fig.13. SEM micrograph of AI for two different spots (a and b).

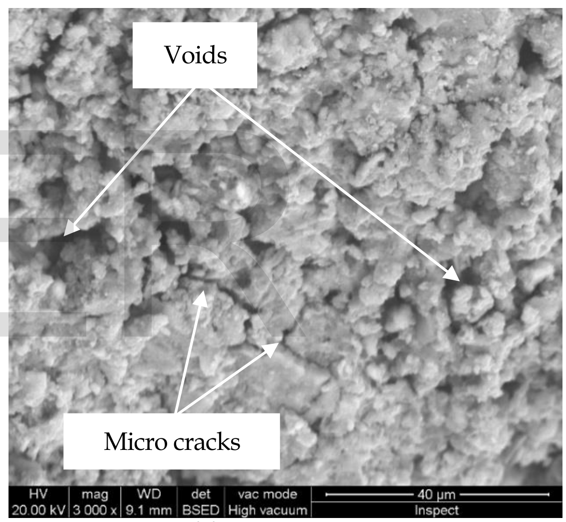


(a) At cement paste

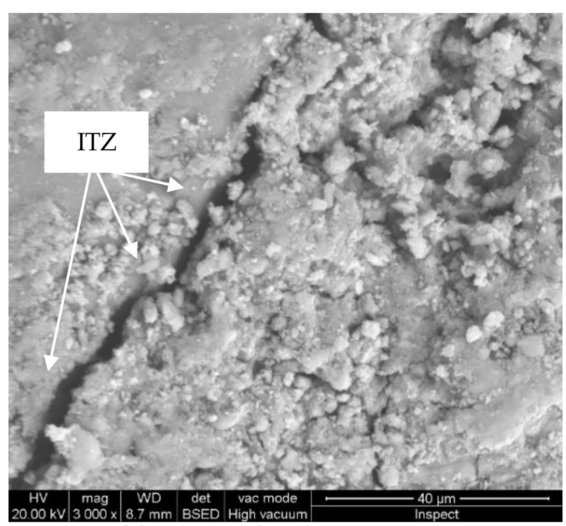


(b) At the interfacial transition zone

Fig.14. SEM micrograph of NI mix for two different spots (a and b).



(a) At cement paste



(b) At the interfacial transition zone

Fig.15. SEM micrograph of PI mix for two different spots (a and b).

5 CONCLUSIONS

The subsequent conclusions were drawn from the experimental work carried out in this research:

1. An amino and ester-based inhibitor (AI) increases the slump to a maximum value between the three inhibitor mixes by 17.39%. The early age compressive strength decreased by 10.36%. The ultimate compressive strength also decreased by 13.49%. The tensile splitting strength decreased by 19.07%. The bond strength decreased by 4.24%.
2. A nitrite-based inhibitor (NI) decreases the slump by 13.04%, in which it is the least affected mix between the three inhibitor mixes. The early age compressive strength decreased by 5.03%, while the ultimate compressive strength increased up to 5.25%. The tensile splitting strength decreased by 10.17%. The bond strength is slightly decreased by 1.33%.
3. A phosphate-based inhibitor (PI) decreases the slump to a maximum value between the three inhibitors mixes by 39.13%, which indicates the worst workability between the three inhibitors. The early age compressive strength decreased by 20.16%. The ultimate compressive strength also decreased by 19.86%. The tensile splitting strength decreased by 11.44%. The bond strength decreased by 30.42%.
4. These results open the possibility of using a nitrite-based inhibitor (NI) due to the good effect of this inhibitor on concrete compressive strength and the least bad effect on other mechanical properties of concrete.
5. SEM showed the good effect of nitrite-based inhibitor (NI) on the microstructure of mortar.
6. From all the results it is observed that the optimum inhibitor of the studied three inhibitors is a nitrite-based inhibitor (NI).

6 RECOMMENDATIONS FOR FURTHER WORK

This research was limited on studying three inhibitors. Therefore, the effect of adding corrosion inhibitor admixtures on concrete properties and steel reinforcement needs to be studied on more inhibitors. Testing the influence of different parameters like the concrete cover and chloride percentage is also recommended.

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