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Self-healing Concrete Using Microcapsules Containing Mineral Salts

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ABSTRACT

Propagating micro-cracks in a structure decreases its load-bearing capacity and leads to the collapse of the entire structure. Addition of various additives in all kinds of concrete or concrete ingredients, as several studies have shown, could significantly make concrete reclaim from the specifications and attributes point of view. A possible manner to the common ruin and expensive preservation of concrete infrastructure, utilizing encapsulating healing factors is helpful for the self-healing of concrete. The self-healing concrete with microencapsulated Preyssler, and calcium nitrate was studied in this paper. Microcapsules were synthesized by in-situ polymerization of urea-formaldehyde as a shell around the core materials inclusive of Preyssler, calcium nitrate. Physicochemical characterization of microcapsules was conducted by Fourier transformation infrared spectroscopy, field emission scanning electron microscopy, and Transmission Electron Microscope. The mechanical assessment of cementitious specimens with different dosages of microcapsules (0%,0.5%, 1%, 1.5%, and 2%) was performed by compressive tests. Also, by measurement before and after damage after 10 days, the self-healing potential was tested. After the concrete was damaged by exerting 30% of its final load, all samples were incubated by immersion in water. According to the results, the sample containing 0.5% UFN, the sample containing 1.5% UFP, and the sample containing 1.5% UFNP have higher repair rates than others. This scope of research because of its interdisciplinary nature would own several possibilities to be pioneering with making an opening gate to link sciences and engineering such as material, chemistry, science, nanotechnology, and the field of engineering to persuade a wide spectrum of contribution in engineering sciences and usages.

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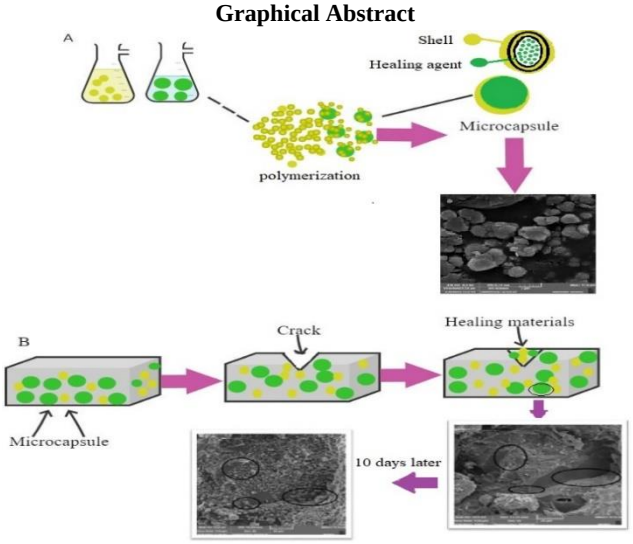
Graphical Abstract



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NOMENCLATURE

P	Preyssler	SEM	Scanning electron microscopy
CN	Calcium Nitrate	TEM	Transmission Electron Microscope
UFN	Urea-formaldehyde calcium nitrate microcapsule	FT-IR	Fourier transform infrared spectrometer
UFNP	Urea-formaldehyde calcium nitrate-Preyssler microcapsule	EDS	Energy Dispersive Spectroscopy
UFP	Urea- formaldehyde Preyssler microcapsule		

1. INTRODUCTION

One of the essential building materials used in most of the sections of structures is concrete. Existing crack in concrete structures is so harmful for durability and reliability (1, 2); commonly, this event begins at the atomic area with defects that get more significant and larger that create cracks. In concrete structures, protecting them is controlling and stopping crack diffusion, increasing their yield and dependability, and extending their service lifetime. So, self-healing concrete is an answer for good bases because it may forbid the growth of early life micro cracks into more significant cracks. Without needing human or any kind of manual interference, self-healing materials automatically heal damage (3-5). From the past till today, Micro and Nano-encapsulation are challenging techniques in protecting drugs and healing agents (6, 7). Microcapsule-based self-healing concrete is a novel kind of concrete material that repair micro cracks in concrete and reclaim the strength and stability of concrete (8). The repairing origin of microcapsule self-repairing concrete is typical that when micro cracks of concrete develop and tangency with the microcapsules, the shell of the microcapsules fracture, and the epoxy resin diluted moves into the crack and responds with the curing factor. This fills the cracks and arrives at the target of repairing the cracks (9, 10). Today, researchers have done empirical and simulation investigations on microcapsule-based self-healing concrete. Its efficiency, like its stability compared with ordinary cement, has been of interest to many researchers, and several studies have been carried out on its empirical aspects (11-14). White et al. (9) are the first researchers that report a feasible display of self-healing materials through implanting encapsulated healing agents into a polymer matrix, including diffused catalysts. de Souza Rodrigues et al. (15) investigated the synthesis, characterization, and self-healing qualitative valence of polyurethane microcapsules that include toluene diisocyanate and isophorone diisocyanate as a core factor. The thermal analysis they were determined that the decreasing temperature of the material was higher in TDI-including microcapsules as the core factor. Development and mineralization specifications of *Bacillus subtilis* (BS) detached from marine aquaculture wastewater and its usage in coastal self-healing concrete was investigated by Fu et al. (16). In the research of Wang et al. (17), the strength recovery and acoustic performance of microcapsule self-healing concrete were used as evaluation indices to assess the damage to the microcapsule self-healing system. They concluded that the self-healing performance was better for the microencapsulated self-healing concrete than the ordinary concrete. Self-healing techniques involve the use of microcapsules containing self-healing agents and catalysts that are dispersed within a structure. In the event of excess load or damage to the structure, the microcapsules detect the damage and release the self-healing agent stored inside them. The self-healing agent then reacts with the previously dispersed catalysts, effectively repairing the damage. Therefore, a stable manufacturing method for the microcapsules containing self-healing agents is crucial in order to repair the damage and ensure the structural stability. Self-healing microcapsules must possess sufficient mechanical strength and thermal stability to be effectively utilized for the repair of composite structures. These properties can be affected by various manufacturing conditions, such as constituent materials, stirring speed, pH, and reaction temperature (18, 19). The speed at which a mixture is stirred is a crucial factor in determining the size and size distribution of microcapsules. The size of these capsules is directly related to their strength. A study by Kosarli et al. (20) examined the mechanical properties, thermal stability, and healing efficiency of microcapsules with five different average diameters, by controlling the stirring speed. The researchers found that microcapsules with smaller diameters showed better thermal stability and lower degradation of mechanical performance.

The different healing factors for crack-healing in cement-based products are displayed in Figure 1 (21). Also, Figure 2 shows that microencapsulation is the most well-known technique accepted for releasing healing components into cement-based products. As we know, for producing concrete with the boosted qualification, utilizing inorganic additives has possessed more consideration worldwide. One of the novel, the environmentally friendly tasks is extending the region of the inorganic additives of compound function via the utilization of heteropolyacids. Heteropolyacids are propounded as a type of inorganic clusters that are built of hydrogen, oxygen, and some transition metals and non-metals (22, 23). In Figure 3, one of the famed forms of heteropolyacids is named Preyssler structures, shows its general formula of it is $[NaP_5W_{30}O_{110}]$ [14]. Several researchers investigated the positive factors of organic polymer concrete materials on attributes of concrete. Some of the attributes include excellent vibration

damping, high compressive strength, great vibration damping properties, high particular stiffness and strength, resistance to corrosion and chemicals , fast curing, and the capacity to create involved shapes (24-26). Based on a brief literature review, it has been found that multicomponent concrete with several additives has emerged as a new generation of concrete that is able to maintain the required properties in all operating conditions. The use of multicomponent concretes is growing due to their ability to manage structure formation and show directed quality in properties at all stages of technology (27, 28). For example, Balamuralikrishnan et al. (29) analyzed the flexural, shear, and combined effects of the flexural and shear behavior of reinforced concrete beams that were strengthened with externally bonded ferrocement laminates made with spent catalysts. They compared the results of these beams to control beams that were not strengthened. The testing was conducted under two-point loading conditions. Mohammed et al. (30) investigated how steel fiber-reinforced concrete flat slabs perform when subjected to punching shear force. The experimental results showed that slabs incorporating steel fiber had a 21.8% higher punching shear capacity compared to those without steel fiber. Additionally, the slabs reinforced with steel fiber demonstrated greater ductility than the ones without fiber reinforcement. Nistratov et al. (31) conducted research on waste carbon plastics and unused industrial fiberglass plastics, including office equipment components that contained highly dispersed fibers and laminating coatings with an organo-mineral matrix. The study revealed that adding 1% by weight of fibers to slag blocks and active carbon pellets significantly increases their compressive strength, but the bending strength remains unchanged due to the dispersed reinforcement. As an admixture contributes to the acceleration of the hydration of cement and helps, the increase of the strength of concrete over the long term is calcium nitrate. In our literature survey, we discovered that Polyoxometalates - clusters of early transition metals have not yet been used in concrete microcapsules, specifically Preyssler heteropolyacid (HPA). Given our experience with HPAs and related chemistry (32) and cited references therein), we were inspired to begin investigating this area further. We recently explored the application of different polyoxometalates and Preyssler polyoxometalate in nanotechnology (33), and with our ongoing interest in extending the applications of Preyssler, we feel it is important to examine the potential benefits of using this heteropolyacid as a microcapsule to improve the compressive strength of concrete.

So, moderate dosages of 0.5% to 2% by weight of cement are required to get these advantages. In this paper, the main aim is to evaluate the application of CN, and P that are mineral salt as a healing operators and to define their efficacies in self-healing mechanisms for concrete materials. To gain this aim, a laboratory test was done to measure the self-healing ability of concrete with CN and P microcapsules and compare the results with samples without microcapsules. In Figure 4 a diagrammatic microcapsule-based self-healing method is displayed.

2. EXPERIMENTAL PROCEDURE

The experimental scheme is shown in Figure 5.

2. 1. Materials Calcium nitrate and Preyssler were used to create UFN, UFP, and UFNP microcapsules. Raw materials used for the experiments have been listed in Table 1.

2. 1. 1. Synthesis of Preyssler In a 250 ml beaker, dissolve 99 g of dihydrate sodium tungstate in 120 ml of distilled water with temperature control between 40-45 °C while stirring, then slowly add 75 ml of phosphoric acid 85% to it and it was refluxed for at least 5 hours. After the reflux period is over, add 5.22 g of KCl salt gradually at room temperature, and at the end, the solution is stirred for 30-40 minutes.

The green precipitate is filtered and crystallized in a minimum amount of water at 70 °C. In the first step, the

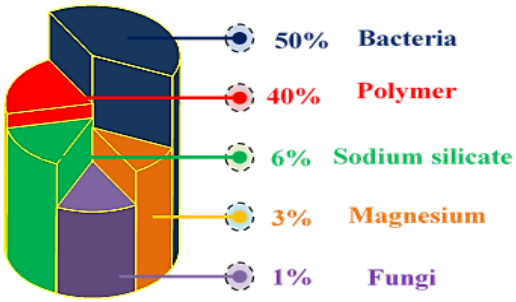


Figure 1. Different methods utilized for the search phrase 'concrete self-healing' event in the Scopus database

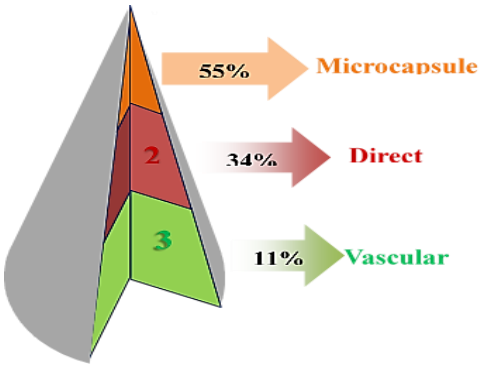


Figure 2. Different techniques of transporting healing factors into the cement-based products for search phrase results in the Scopus database

white crystals of preyssler anion appear on the solution`s surface and are separated from the environment by filtering. Figure 6 showed the produced preyssler.

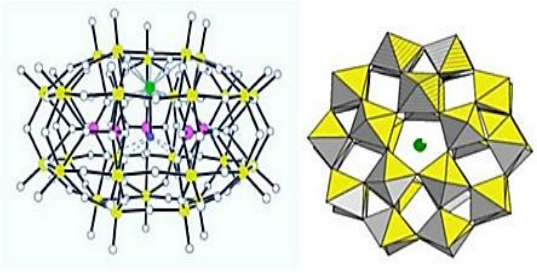


Figure 3. Preyssler [40]

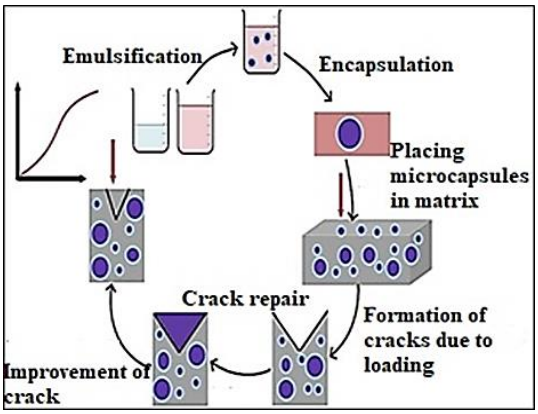


Figure 4. Schematic representing microcapsule-based self-healing method

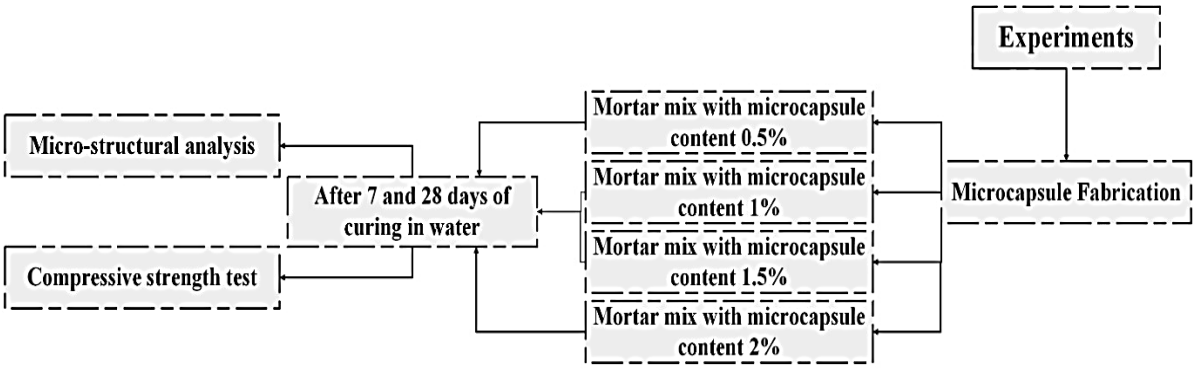


Figure 5. Experimental plan

TABLE 1. Raw materials utilized for the tests

Material Name	Formula	Usage	Pure degree	Manufacturer
Resorcinol	C6H6O2	Preparation of Microcapsules	99.0 %≤	MERK CO
Formaldehyde	CH2O	Preparation of Microcapsules	37%	MERK CO
Ammonium Chloride	NH4Cl	Preparation of Microcapsules	99%	MERK CO
Urea	CO (NH2)2	Preparation of Microcapsules	99%≤	MERK CO
Hexane	$CH_3 (CH_2)_4CH_3$	Preparation of Microcapsules	85%<	MERK CO
Sulfonic Acid	R-C6H6-OSO3H R=C10-C13	Preparation of Microcapsules	96%	MERK CO
Span 60	$C_{24}H_{46}O_6$	Preparation of Microcapsules	AR	MERK CO
Calcium Nitrate Tetra hydrate	$Ca (NO_3)_2 \times 4 H_2O$	Preparation of Microcapsules	99-102%	MERK CO
Sodium tungstate dehydrate	Na2WO4.2H2O	Preparation of preyssler	AR	MERK CO
Phosphoric acid	H3PO4	Preparation of preyssler	85%	MERK CO
potassium chloride	KCL	Preparation of preyssler	90%≤	MERK CO

2. 2. Synthesis of Microcapsules The procedure, which uses an in-situ polymerization chemical process to encapsulate CN and P under a water-in-oil emulsion, includes aqueous and continuous phases. The aqueous phase consists of urea, formaldehyde, resorcinol, ammonium chloride, and calcium nitrate as core materials dissolved in distilled water. In general, the synthesis of self-healing microcapsules is based on the under proceedings.

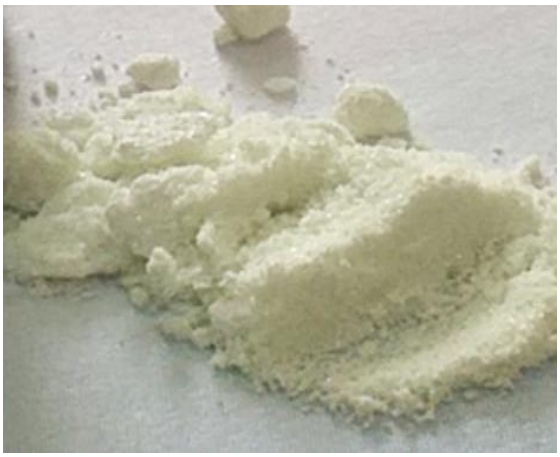


Figure 6. Produced Preyssler

First emulsification, as the aqueous CN, and P are spread into the needful particles, then these spread particles are caught in a shell frame as a result of a chemical response between the surfactants. This act is recognized as polymerization. The synthesis of microcapsule, as introduced in the next part, followed the action reported in literature (34). Figure 7 displays the stages involved during microcapsule making and the final product.

2. 2. 1. Calcium Nitrate Self-healing Microcapsules The procurement method for microcapsules, including CN, was based on prior studyconducted by Hassan et al. (34), utilizing a water-in-oil suspension polymerization way that urea formaldehyde is as a shell material. The monomer phase was built of the microcapsules' shell materials and CN as a healing factor.

Part A: For making an aqueous solution containing 0.5 g Resorcinol, 0.5 g Ammonium Chloride, 5 g Urea, 13 g Formaldehyde, and 10 g Calcium Nitrate Tetra hydrate that all of them were mixed in 50 ml of water and stirred at 750 rpm for 1-3 h.

Part B: For making the oil phase (continuous phase), 180 g of hexane with 0.5 g span60 and 0.1g sulfonic acid were mixed at 800-1500 rpm for 24 h at 40 °C. Then, the obtained solution was ultrasonicated for 10 min at 50% amplitude in a pulse regime. The catalyst in this procedure was sulfonic acid, which has a straight effect on the rate of reaction. The reason of utilizing Hexane in the oil phase was cheap and light of it. When it is placed under a vapor hood, its volatility is so helpful because for the collection of the microcapsule, the evaporation and removal of hexane are simple. To ensure that a water-in-oil emulsion was done, it is crucial to protect the ratio between the water and the oil at about 1:3. The oil phase was heated at the preferable temperature between 40-50°C and agitated via a high-shear mixer. Utilizing the high temperatures are forbidden since the temperature straightly acts on the rate of response and is the reason for the premature formation of the shell wall. The aqueous phase was added dropwise when the temperature was desired, and the polymerization procedure began. The heating time varied from 1-3 h to completion of the in situ condensation of the urea–formaldehyde and also to turn the liquid droplets in the aqueous phase into microcapsules with a solid polymer shell. After the ending of the response, the hexane was discharged, and then the microcapsule slurry was filtered. In the next part, the filtered microcapsules were dried in an oven for two days (48 h) at temperature of 50°C.

2. 2. 2. Calcium Nitrate-Preyssler Self-healing Microcpsules For the synthesis of UFNP, a ratio of 50-50% of CN and P are added to the aqueous solution. All the chemical materials for the aqueous solution were like the synthesis of calcium nitrate microcapsules. Also, the oil phase was similar to the synthesis of UFN.

2. 2. 3. Preyssler Self-healing Microcapsules The method of synthesis of microcapsules containing P is the same as the method of synthesis of microcapsules of calcium nitrate, with the difference that in the aqueous phase, instead of CN, P was added as the core material of the microcapsule.

2. 3. FTIR Analysis FTIR analyses of the specimens were built by utilizing Fourier transform infrared spectrometer in the range 400–4000 cm^{-1}. FTIR spectra of the CN and P, and their microcapsules are presented in Figures 8-10, respectively. The vibrational band in the area of 3350 cm^{-1} is related to the tensile bond of H-O and H-N in urea formaldehyde polymer. By comparing the FT- IR spectra of UFN containing it, it can be concluded that the presence of a typical peaks of 833.2 and 1383.46 cm^{-1}. in CN and microcapsules is evidence of the presence of CN in the urea-formaldehyde microcapsules. By comparing the FT-IR spectra of the P and the microcapsule containing it, it can be concluded that the presence of common peaks of 517.68 and 1164.45 cm^{-1}. in the P and microcapsule is evidence of the presence of the P in the urea-formaldehyde microcapsule. Also, by comparing the FT-IR spectra of CN-P, and microcapsules containing them, it can be concluded that the presence of a common peak of 3347.18 cm^{-1}. in CN and prescribers and their microcapsules is evidence of the presence of these two substances in urea-formaldehyde microcapsules.

2. 4. SEM Analysis The microcapsules and concrete structure were done utilizing a Field Emission Scanning Electron Microscope (LMU TESCAN BRNO-MIRA3) operated. Before to used SEM imaging, splashing the gold powder was performed on the samples. According to Figure 11, most of the microcapsules have spherical shaped, while the particles with irregular shapes can be

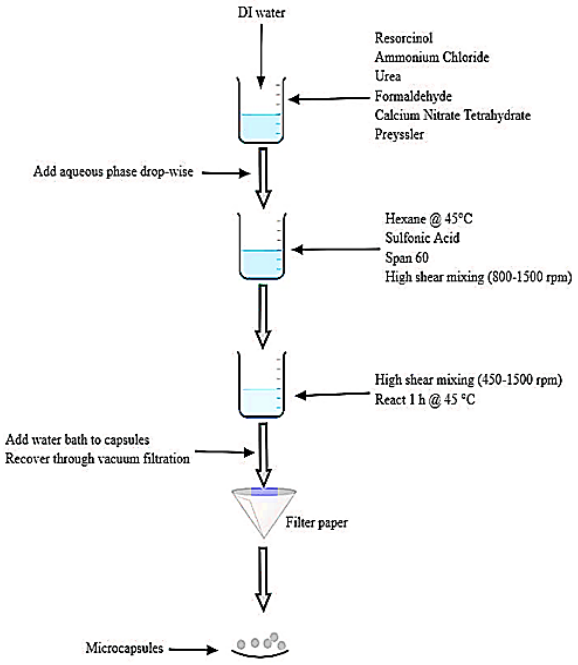


Figure 7. Microencapsulation synthesis process

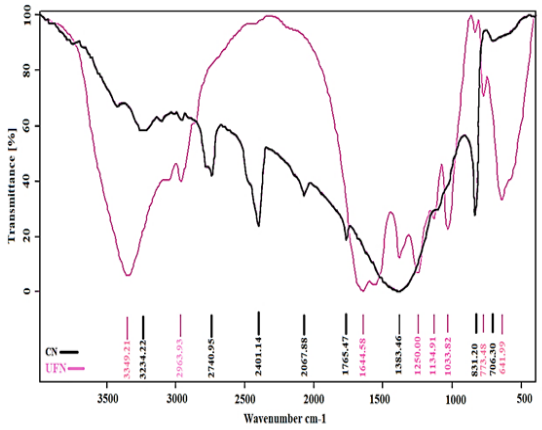


Figure 8. FT-IR spectrum of CN and its microcapsules

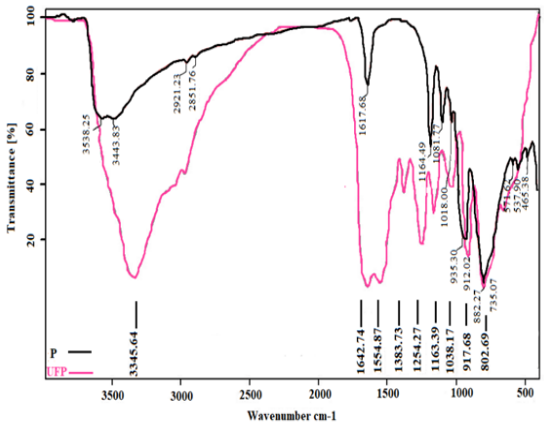


Figure 9. FT-IR spectrum of P and its microcapsules

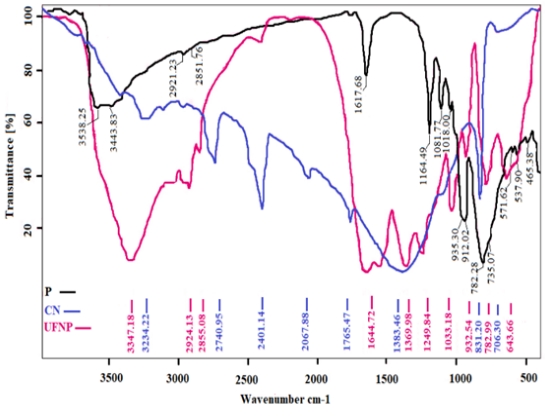


Figure 10. FT-IR spectrum of CN-P and their microcapsules

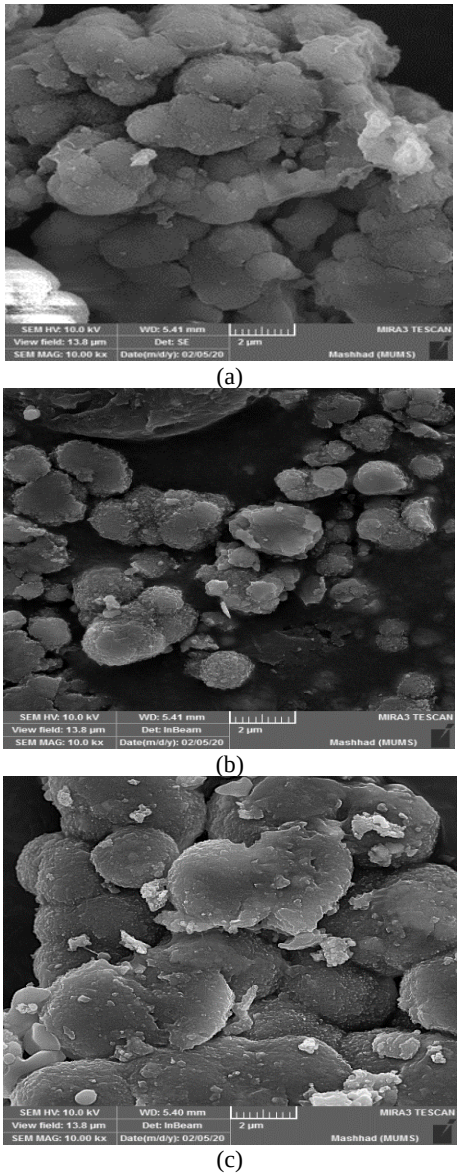
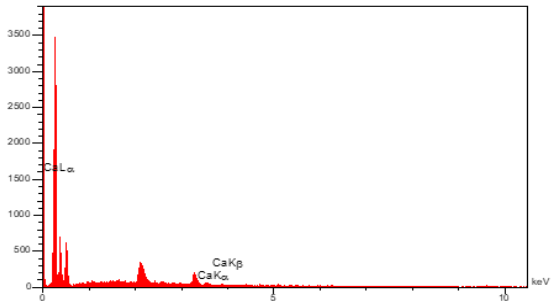


Figure 11. FESEM images of microcapsules: (a) UFN, (b) UFP, (c) UFNP

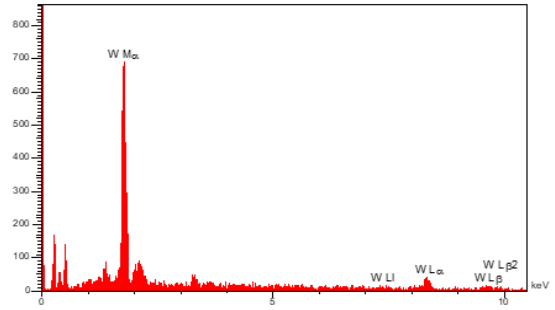
found between them. Also, from the EDS analysis can understand that the UFN consists of Ca, O, Na, and C elements.

Therefore, it revealed the existence of urea-formaldehyde (shell material) and nitrate calcium (core material). As shown in Figure 12a, given that the calcium peak intensity in the EDS analysis chart is very high. It can be concluded that the nucleus of the microcapsule contains CN and is well-formed. From the EDS of the UFP, understand that it consists of W, O, N, P, and C elements. Therefore, it revealed the existence of urea-formaldehyde (shell material) and Preyssler (core material). According to Figure 12b, considering that Tungsten (W) is the main constituent of Preyssler and has a high peak, it can be concluded that the core of the microcapsule has an active substance and is well-formed. The EDS of the UFNP shows that it consists of W, Ca, O, N, and P elements. Therefore, it revealed the existence of urea-formaldehyde (shell material) and calcium nitrate- Preyssler (core material). According to Figure 12c, considering that Tungsten (W), the calcium (C), which are the main constituent of Preyssler and calcium, respectively, has a high peak, it can be concluded that the core of the microcapsule has an active substance and is well formed.

2. 5. TEM Analysis TEM observation of the microcapsules was made using a Transmission Electron Microscope (LEO912 AB) operated. This analysis was done to ensure the reliability of producing spherical microcapsules. TEM images of microcapsules are demonstrate in Figure 13.



(a)



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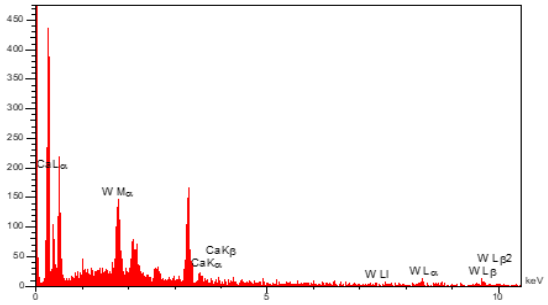
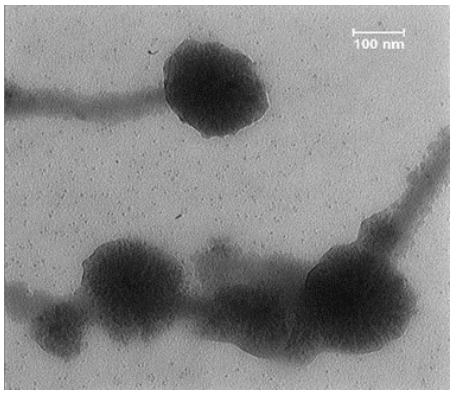
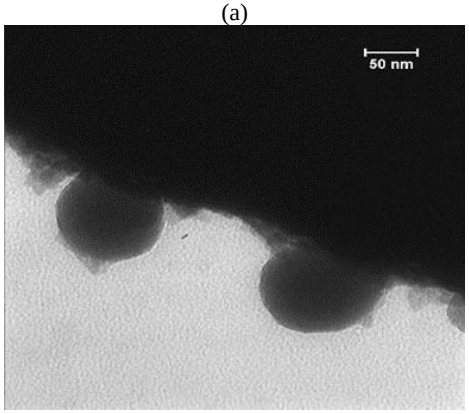


(c)

Figure 12. EDS analysis: (a) UFN, (b) UFP, (c) UFNP



(a)



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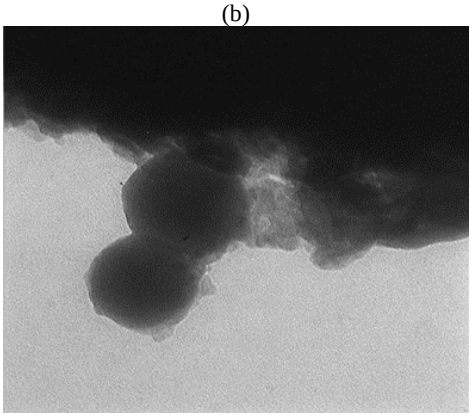


(c)

Figure 13. TEM images of microcapsules: (a) UFN, (b) UFP, (c) UFNP

2. 6. MIX Design For mix design, we utilized concrete's design process that has a water/cement ratio of 0.23. The amount of materials for the mix design are offered in Table 2. In the present study, the mixing steps are as follows:

1. The weight of all consumables was accurately measured based on the desired percentages.
2. All superplasticizers were mixed with all water consumption.
3. All dry materials were mixed with a mixer for 5 min.
4. By adding 65% of water and lubricant mixture, the materials inside the mixer were mixed at a speed of 1000 rpm for 3 min.
5. The remaining water and superplasticizer were added, and mixing was continued at 1000 rpm for 8 minutes.
6 - Finally, the synthesized microcapsules are added to the mixture.

In the next step, the concrete nanocomposites were poured into lubricated molds, and the samples were numbered.

2. 6. 1. Curing Regime The specimens were covered via wet sackcloth for 24 h. The drinkable water immersion at room temperature was selected for the curing regime to enable healing.

3. RESULTS AND DISCUSSIONS

3. 1. Testing of Self-healing Concrete We utilize the microcapsules, including CN, P, as the healing factors in the matrix of concrete to evaluate their self-healing. The efficacy of the number of microcapsules to recognize the excellent condensation by weight of cement was investigated. The concentration experimented were 0.5%, 0.1%, 1.5%, and 2.0%. According to the ASTM C109 standard, compressive strength tests were done for specimens with or without microcapsules, and the cubic testes had dimensions of 50 mm × 50 mm × 50mm.

3. 2. Concrete Compressive Strength To evaluate the compressive strength of specimens after 7 and 28 days of curing in a humidity chamber was conducted, and the efficacy of the microcapsules on the standard properties of the concrete was evaluated. The average testing results of three samples of each design samples are listed in Figures 14-16, which showed that the number of microcapsules have a significant impact on compressive strength. Considering that the compressive strength of concrete has a direct relationship with the density of concrete, it can be said that the denser the concrete, the higher its compressive strength. For example, according to Figures 17-19, which shows the density of samples with different weight percentages of microcapsules (0, 0.5, 1, 1.5, 2), in the sample containing UFN from 1% to2%, the density of the samples It has no microcapsules more than the sample.

Also, the sample containing 0.5 and 2% UFP and the samples containing UFNP in the range of 0.5 to 1.5% have a higher density than the sample without microcapsules. For this reason, it can be concluded that the higher the density value, the higher the density of the sample and the higher the strength.

TABLE 2. Mix design

Material	Amount in 1 kg/m^3
Cement(kg)	840
Water(kg)	200
silica sand(kg)	1104
Admixture 1 (Superplasticizer)	42
Admixture 2 (Microcapsule concentration[1] (%))	0.5,1,1.5 and 2%
Micro silica	202

[1] Concentration is given as a percentage by weight of cement

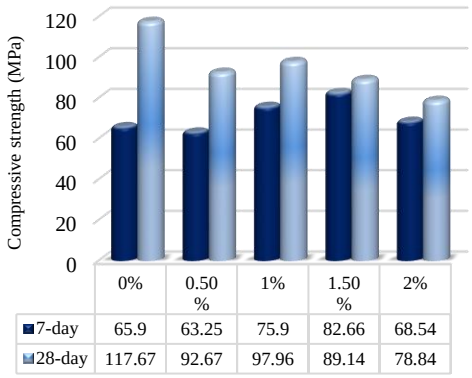


Figure 14. Compressive strength of concretes containing UFN at different ages

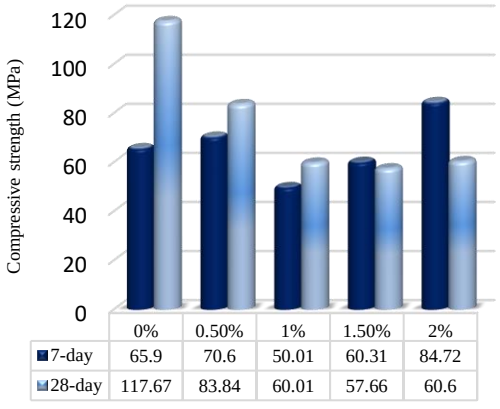


Figure 15. Compressive strength of concretes containing UFP at different ages

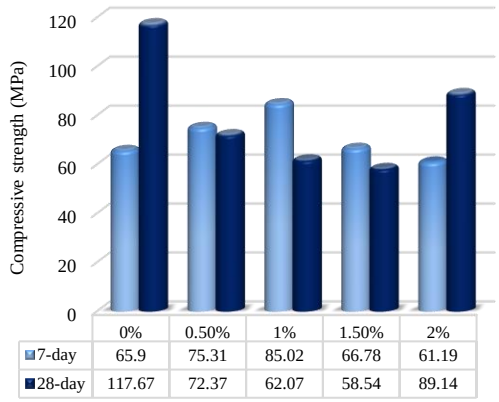


Figure 16. Compressive strength of concretes containing UFP at different ages

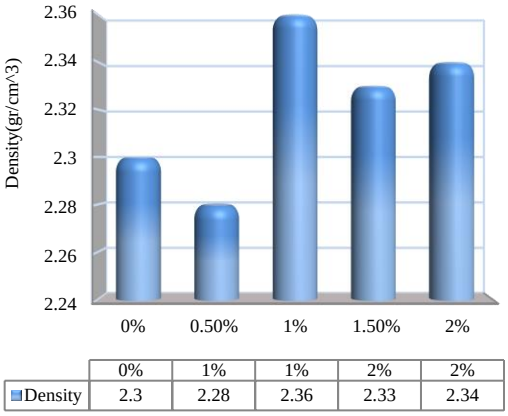


Figure 17. Density of samples with different percentages of UFN

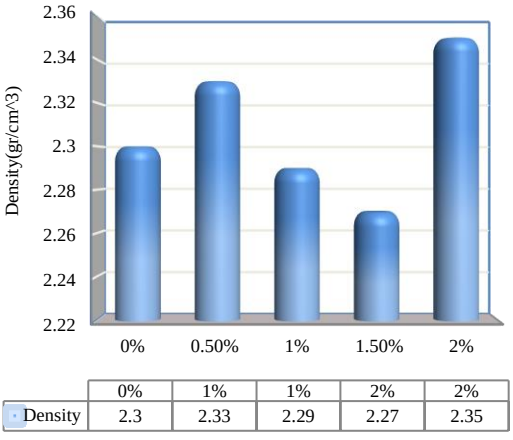


Figure 18. Density of samples with different percentages of UFP

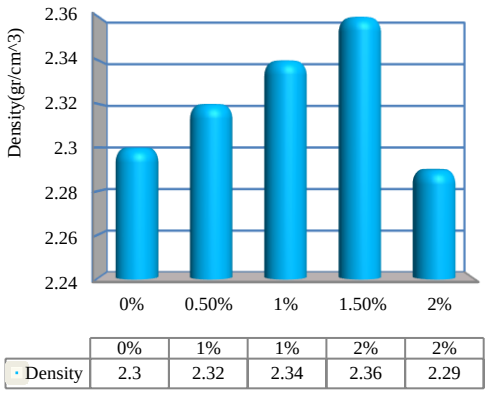


Figure 19. Density of samples with different percentages of UFNP

Figures 20 and 21 compare 7 and 28-day compressive strength performance of concrete samples containing various microcapsules. According to the figures, the following results can be inferred.

- The concrete sample containing 0.5% UFN has the greatest 7-day compressive strength compared to the other types.
- The concrete sample containing 1% UFN has the greatest 7-day compressive strength compared to the other types.
- The concrete sample containing 1.5% UFN has the greatest 7-day compressive strength compared to the other types.
- The concrete sample containing 2% UFP has the greatest 7-day compressive strength compared to the other types.
- The concrete sample containing 0.5% UFN has the greatest 28-day compressive strength compared to the other types.
- The concrete sample containing 1% of UFN has the greatest 28-day compressive strength compared to the other types.
- The concrete sample containing 1.5% UFN has the greatest 28-day compressive strength compared to the other types.
- The concrete sample containing 2% UFNP has the greatest 28-day compressive strength compared to the other types.

3. 3. Recovery of Compressive Strength of Concrete Samples Containing Various Microcapsules In order to check the final compressive strength after repair, other concrete samples containing different percentages of microcapsules were damaged after a 28-day curing period with 30% of the final loading obtained in the previous section. At first, a group of concrete samples were damaged for 2 h. The water was kept at room temperature until the repair

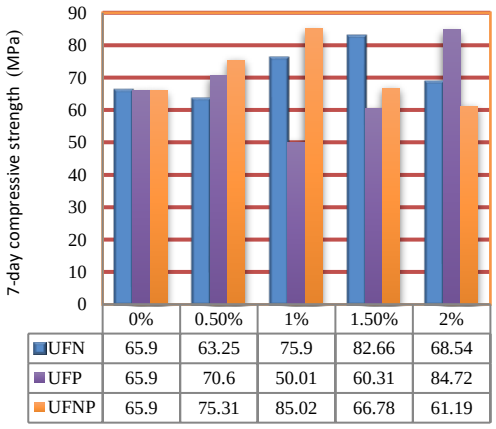
process was established. After 2 h, the samples were again loaded and broken, and their resistance was considered as the initial strength of the repair. Another group of concrete specimens were situated in water for 10 days to make the repair procedure more complete, and their resistance was considered the final strength of the repair was recorded.

To obtain the recovery rate, the relationship introduced by Dong et al. (35) has been used.

$$\textbf{Strength recovery rate}=\frac{\textit{final strength of the restoration}-\textit{Initial strength to repair}}{\textit{Initial strength to repair}}$$

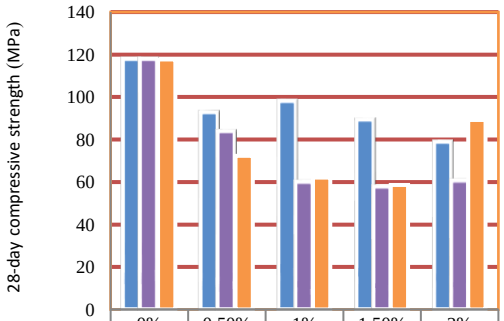
Also, the equation introduced by Li et al. (36) can be used to obtain the amount of resistance restoration.

$$\textbf{Strength recovery rate}=\frac{\textbf{Maximum strength to reloading}}{\textit{Initial strength}}$$



	0%	0.50%	1%	1.50%	2%
UFN	65.9	63.25	75.9	82.66	68.54
UFP	65.9	70.6	50.01	60.31	84.72
UFNP	65.9	75.31	85.02	66.78	61.19

Figure 20. Comparison of 7-day compressive strength performance of concrete samples containing different microcapsules



	0%	0.50%	1%	1.50%	2%
UFN	117.67	92.67	97.96	89.14	78.84
UFP	117.67	83.84	60.01	57.66	60.6
UFNP	117.67	72.37	62.07	58.54	89.14

Figure 21. Comparison of 28-day compressive strength performance of concrete samples including various microcapsules

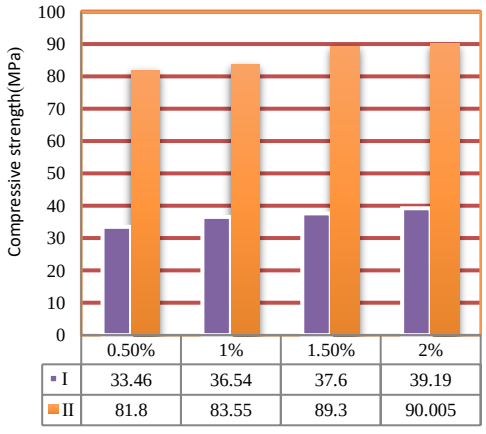
In the following, for example, the compressive strength test results of samples containing UFN, UFP, and UFNP with a loading of 30% of the final load are given.

3. 3. 1. Compressive Strength Test Results of Samples Containing UFN With the Loading of 30% of the Final Loading According to Table 3, it can be concluded that the concrete specimens including 0.5% by weight of UFN, have a higher strength repair rate than other percentages by weight of microcapsules. Also, in Figure 22 the average compressive strength of the samples, containing different percentages of UFN under 30% loading of the final strength is displayed.

3. 3. 2. Compressive Strength Test Results of Samples Containing UFP with the Loading of 30% of the Final Loading According to Table 4, it can be concluded that the concrete sample containing 1.5% by weight of UFP has a higher repair rate than other percentages by weight of microcapsules. In Figure 23, for

TABLE 3. The recovery rate of compressive strength of concrete samples, containing UFN with different percentages under 30% final loading

Percentage of microcapsules	Maximum initial compressive strength (MPa)	Final compressive strength after 10 days of restoration (MPa)	Resistance recovery rate
0.5%	33.46	81.80	1.44
1%	36.54	83.55	1.28
1.5%	37.60	89.30	1.37
2%	39.19	90.005	1.29



	0.50%	1%	1.50%	2%
I	33.46	36.54	37.6	39.19
II	81.8	83.55	89.3	90.005

Figure 22. The average compressive strength of the samples, containing different percentages of UFN under 30% loading of the final strength (MPa): (I) Initial compressive strength after two hours, (II) Final compressive strength after 10 days of restoration

TABLE 4. The recovery rate of compressive strength of concrete specimens, including UFP with various percentages under 30% final loading

Percentage of microcapsules	Maximum initial compressive strength (MPa)	Final compressive strength after 10 days of restoration (MPa)	Resistance recovery rate
0.5%	44.71	73.54	0.64
1%	37.95	60.04	0.58
1.5%	39.45	70.91	0.79
2%	43.46	75.33	0.73

TABLE 5. The recovery rate of compressive strength of concrete specimens, including UFNP with various percentages under 30% final loading

Percentage of microcapsules	Maximum initial compressive strength (MPa)	Final compressive strength after 10 days of restoration (MPa)	Resistance recovery rate
0.5%	32.36	60.67	0.87
1%	44.93	69.63	0.54
1.5%	36	75.55	1.09
2%	48.02	78.97	0.64

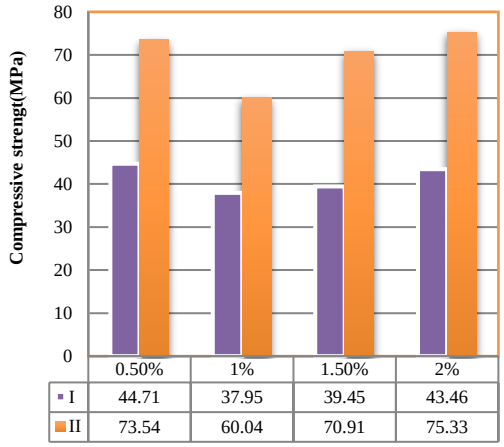


Figure 23. The average compressive strength of the specimens, including various percentages of UFP under 30% loading of the final strength (MPa): (I) Initial compressive strength after two hours, (II) Final compressive strength after 10 days of restoration

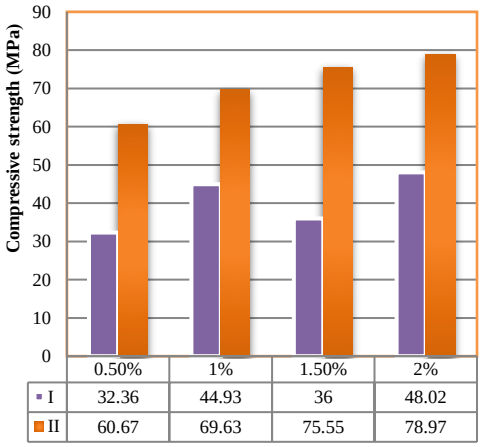


Figure 24. The average compressive strength of the specimens, including various percentages of UFNP under 30% loading of the final strength (MPa): (I) Initial compressive strength after two hours, (II) Final compressive strength after 10 days of restoration

UFP microcapsule, the average compressive strength of the samples under 30% loading of the final strength is showed.

3. 3. 3. Compressive Strength Test Results of Samples Containing UFNP with the Loading of 30% of the Final Loading According to Table 5, it can be concluded that the concrete sample containing 1.5% by weight of UFNP has a higher strength recovery rate than other percentages by weight of microcapsules.

3. 4. Concrete Microstructure After compressive strength analysis, the specimens that expressed the greatest concrete compressive strength of the sample, contained different microcapsules, were analyzed under SEM to evaluate the concrete microstructure and crack repairing process. Figure 24 illustrated the average compressive strength of the specimens, including various percentages of UFNP under 30% loading of the final strength

3. 4. 1. The Repair Process in a Concrete Sample Containing UFN The first sample contains UFN. In this sample, on the first day after cracking, the following cracks were selected so that the repair process could be observed on them after 10 days. As shown in the Figure 25, after 10 days, the specified cracks have been repaired. In Figure 26, EDS is used to show the existence of the repair factor in the crack area. According to the result of the EDS, it can be said that the presence of the Ca element indicates the repair of the crack area by calcium nitrate microcapsules in the cement matrix.

3. 4. 2. The Repair Process in a Concrete Sample Containing UFP The second sample includes UFP. In this sample, on the first day after failure, the following cracks were selected so that the repair process could be observed on them after 10 days (Figure 27). Figure 28 shows the EDS analysis to show the existence of the repair factor in the crack area. According to the result of the elemental analysis, it can be said that the

presence of W and P elements indicate the repair of the crack area by UFP in the cement matrix because these elements are not ordinarily present in cement.

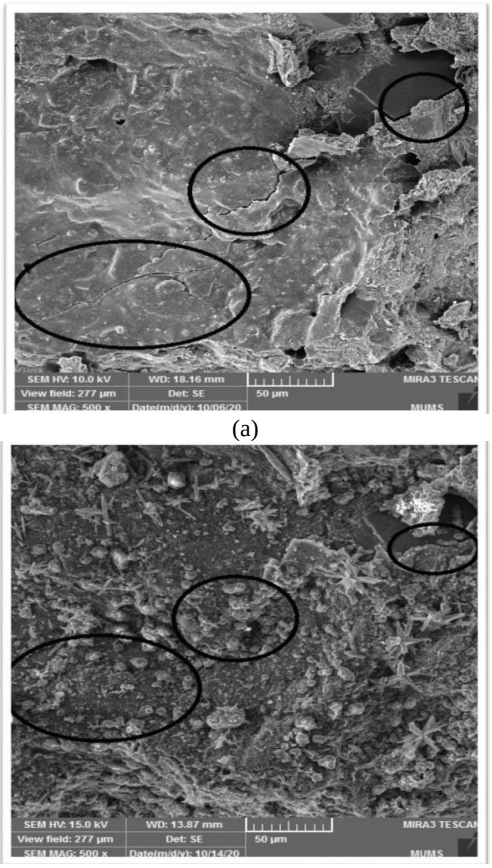


Figure 25. (a) Specifying the number of cracks to check the repair on them, (b) SEM image of crack repair in a sample containing UFN after 10 days

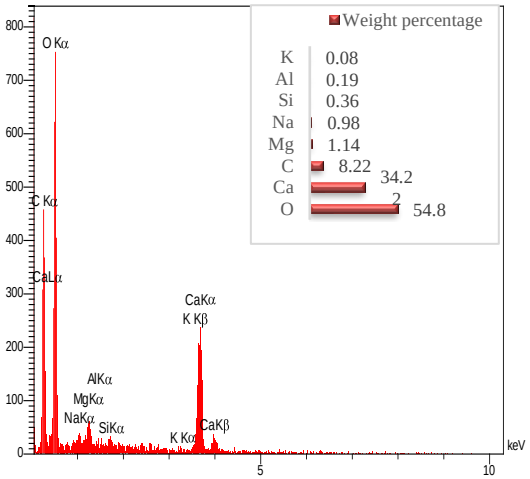
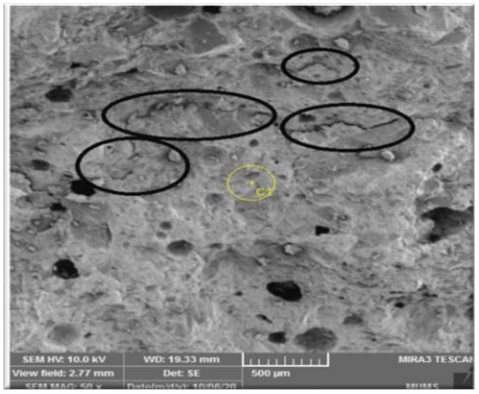


Figure 26. EDS analysis of the cracked area



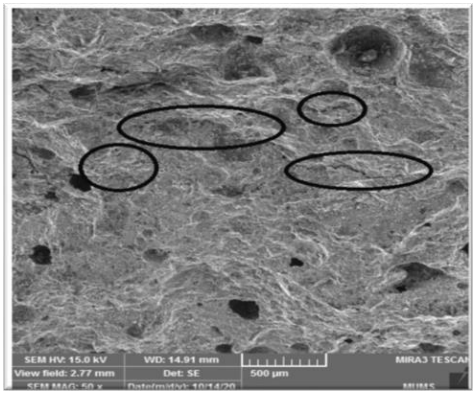


Figure 27. (a) Specifying the number of cracks to check the repair on them, (b) SEM image of crack repair in a sample containing UFP after 10 days

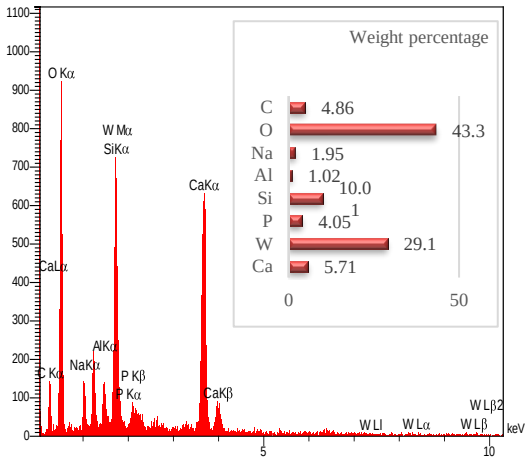
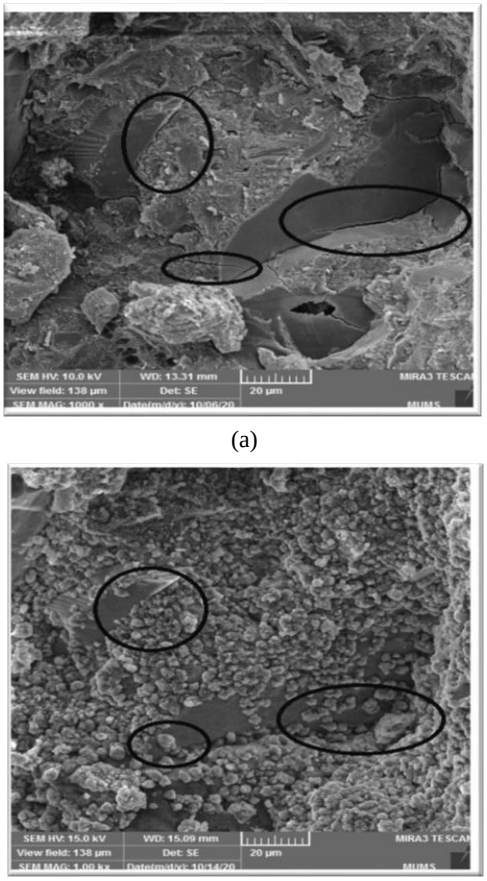


Figure 28. EDS analysis of the cracked area

3. 4. 3. The Repair Process in a Concrete Sample Containing UFNP The third sample includes UFNP. In this example, on the first day after failure, the following cracks were selected so that the repair process

could be observed on them after 10 days (Figure 29). Figure 30 shows the EDS analysis to show the existence of the repair factor in the crack area. According to the result of the elemental analysis, it can be said that the presence of W, P, and Ca elements indicates the repair of the crack area by UFNP in the cement matrix because these elements are not ordinarily present in cement. Also, in Figure 31, the repair of cracks in concrete containing microcapsules is shown.



(a)

(b)

Figure 29. (a) Specifying the number of cracks to check the repair on them, (b) SEM image of crack repair in a sample containing UFNP after 10 days

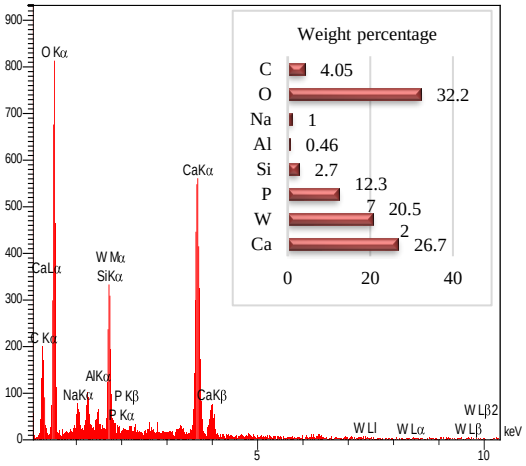
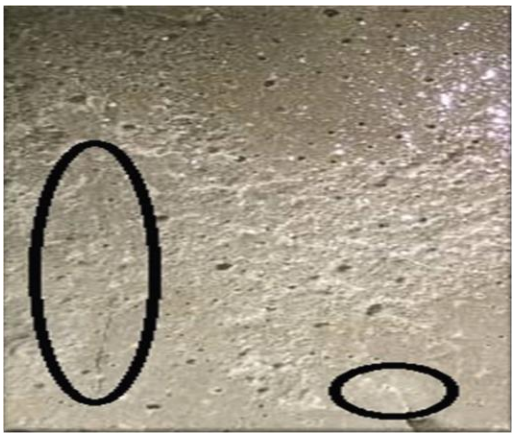


Figure 30. EDS analysis of the cracked area

(a)



(b)

Figure 31. (a) existent the crack, (b) Repair the crack

4. CONCLUSION

In this paper, for self-healing of concrete, the microcapsules were syntheses by an in situ technique utilizing urea-formaldehyde as a shell and mineral salts as the core. The healing yield of concrete by the microcapsules prepared was assessed in terms of the strength restoration as well as the healing microstructure. Some outcomes can be described as follow:

1. Compared to other types of microcapsules, UFN has considerable efficacy in increasing the compressive strength of 7 and 28-day specimens.
2. Among the samples containing UFN, the sample containing 1% microcapsules had the highest 28-day compressive strength, which was 16.75% higher than the

control sample, and the sample containing 1.5% microcapsules, had the highest 7-day compressive strength, 25.44% less than the control sample.

3. Among the samples containing UFP, the sample containing 1.5% microcapsules had the highest 28-day compressive strength, which was 28.75% higher than the control sample, and the sample containing 2% microcapsules had the highest 7-day compressive strength, which was 28.57% less than the control sample.

4. Among the samples containing UFNP, the sample containing 2% microcapsules had the highest 28-day compressive strength, which was 24.25% higher than the control sample, and the sample containing 1% microcapsules had the highest 7-day compressive strength, which was 29.01%. Less than the control sample.

At the end of article can say that the effect of using magnetic water instead of urban drinking water used in this research on the mechanical properties of concrete, including compressive strength, should also be considered by those interested. Also, investigating the effect of using other polyoxometalates as microcapsules can be a very effective suggestion in the continuation of this research.

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Persian Abstract

چکیده

انتشار ریز ترک ها در سازه، ظرفیت باربری آن را کاهش داده و منجر به فروریختن کل سازه می شود. همانطور که مطالعات متعدد نشان داده است، افزودن مواد افزودنی مختلف در انواع بتن یا اجزای بتن، می تواند به طور قابل توجهی از نظر مشخصات و ویژگی ها، بتن را بازیابی کند. یک روش احتمالی مفید برای جلوگیریاز خرابی رایج و حفظ گران قیمت زیرساخت‌های بتنی، استفاده از عوامل التیام‌دهنده کپسوله‌سازی برای خود ترمیمی بتن است. بتن خود ترمیم شونده با پرایسلر و نیترات کلسیم میکرو کپسوله شده در این مقاله مورد بررسی قرار گرفت. میکروکپسول ها با پلیمریزاسیون درجا اوره فرمالدئید به عنوان پوسته در اطراف مواد هسته شامل پرایسلر، نیترات کلسیم سنتز شدند. خصوصیات فیزیکوشیمیایی میکروکپسول ها توسط طیف سنجی مادون قرمز تبدیل فوریه، میکروسکوپ الکترونی روبشی، میکروسکوپ الکترونی عبوری انجام شد. ارزیابی مکانیکی نمونه‌های سیمانی با دوزهای مختلف میکروکپسول (۰، ۰.۵، ۱، ۱.۵ و ۲ درصد) با آزمایش‌های مقاومت فشاری انجام شد. همچنین با اندازه گیری قبل و بعد از آسیب پس از ۱۰ روز، پتانسیل خود ترمیمی مورد آزمایش قرار گرفت. پس از اینکه بتن با اعمال ۳۰ درصد بار نهایی خود آسیب دید، تمام نمونه ها با غوطه وری در آب انکوبه شدند. با توجه به نتایج، نمونه حاوی ۰.۵٪ UFN، نمونه حاوی ۱.۵٪ UFP و نمونه حاوی ۱.۵٪ UFNP نسبت به سایرین نرخ تعمیر بالاتری دارند. این گستره تحقیقات به دلیل ماهیت بین رشته‌ای خود، دارای امکانات متعددی برای پیشگامی در ایجاد دروازه‌ای برای پیوند علوم و مهندسی مانند مواد، شیمی، علم، فناوری نانو و رشته مهندسی برای متقاعد کردن طیف گسترده‌ای از مشارکت در مهندسی و علوم و کاربردها است.