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Metal Nanoparticles and Polymer Incorporated Cement Rock. The Role of Magnetite Nanoparticles in the Mechanical and Bonding Behavior of Portland Cement in Structuring: A Short Review

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Abstract. The changes in the mechanical and physical properties of concrete prepared by incorporating various metal oxide nanoparticles into cement products used in both the oil/gas industry and construction have been analyzed in this review. The study compares the properties exhibited by transition metal oxides and some metal nanoparticles in both isolated and complex forms with polymers in concrete. Analyses were conducted primarily in the direction of changes occurring in properties due to the addition of metal oxide nanoparticles, such as magnetite Fe_3O_4, TiO_2, ZnO, Fe_2O_3, Ag, CuO, TiO_2/SiO_2, Al_2O_3, ZrO_2, core/shell Fe_3O_4/SiO_2, in dispersed form as cement powder or water. It has been shown that appropriate changes occur in properties such as compressive and flexural strength, adhesion, initial and final setting, water absorption, porosity, electrical conductivity, and degradation when metal oxide nanoparticles are added to cement. The density and size of nanoparticles affect their response to various influences, alongside the fundamental properties of the material.

Introduction

Research on nanostructured materials and their applications continues to expand rapidly in sectors such as oil and gas, electronics, biotechnology, pharmacology, and construction industries. The nanosized form of a matter exhibits unique new properties either independently or in composite form due to its high surface energy. In recent years, extensive research and reviews have focused on metal and metal oxide nanoparticles, as well as their complex interactions with polymer macromolecules [1].

There is no field of science and technology where metal nanoparticles are not applied. Particularly highlighted are industrial sectors such as oil and gas fields and the construction sector. In the oil and gas industry, the use of cement products for the cementation of well zones for water and sand isolation has long been recognized as the most promising technology [2]. Furthermore, the irreplaceable nature of cement in construction and the improvement of cement quality through the addition of various additives have been extensively analyzed in review studies by I.P. Segura [3] and others.

It is known that, depending on the application site, the main controlled properties of cement products include: compressive and flexural strength, adhesion, initial and final values of setting, spreadability, water absorption, porosity, and flowability. Specifically, parameters such as electrical conductivity, light reflectance, and resistance to biological effects are sometimes crucial. For many years, additives have been used at the molecular scale to control these properties [4]. However, the rapid advancement of nanoscience has also made a significant impact in this field, with nano-sized modifying agents achieving superior performance [5].

Based on the above, this review analyzes the physical and mechanical properties of concrete obtained by incorporating various transition metals, their polymer composites, as well as binary core/shell nanoparticles into cement solutions. Also, the methods of filling the more commonly used magnetite nanoparticles into concrete, their distribution in their structure, their interaction with the particles, and the changes caused to the main indicators were compared. In addition, the potential for creating smart concrete systems using certain metal nanoparticles' sensitivity to the environment is extensively discussed and aligned with ongoing research conducted by the authors. Also, the current studies include X-ray and infrared spectroscopic analyses of structural changes resulting from the addition of polymer/magnetite nanoparticles to concrete.

Nanoparticles in Cement and Concrete Research

In cement research, it is known where the need to add nano-sized additives actually arises. It is a fact that the production of 1 ton of Portland cement requires 1.6 tons of raw materials and releases 0.8 tons of CO_2 into the atmosphere [6]. By replacing a certain part of the cement component with other additives, it is possible to reduce the consumption of raw materials (which in itself reduces carbon dioxide emissions) and to achieve innovations in quality. This trend can be observed in the statistics of publications dedicated to research conducted over the past 22 years, focusing both broadly and specifically on the addition of nanoparticles to cement [Fig. 1].

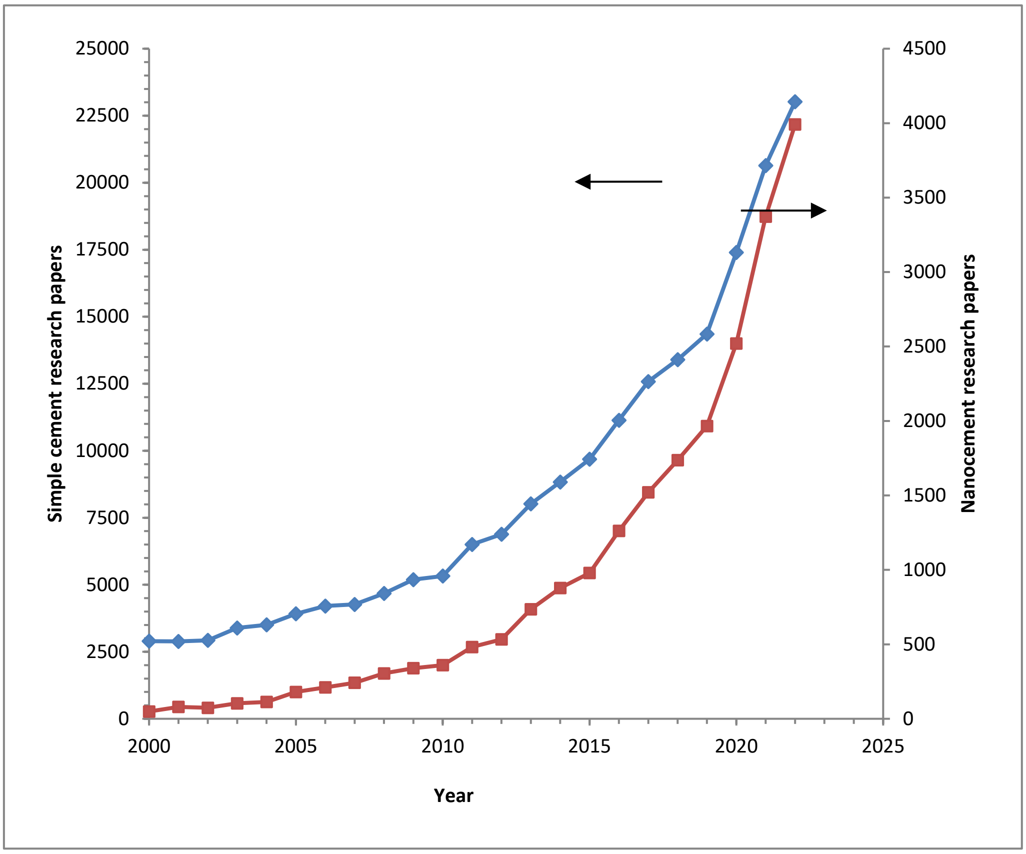

Fig. 1. Chronology of research on cement in the past 22 years.

As can be seen, research in both conventional and nanoparticle modifications of cement has seen a sharp increase since 2010. Statistical analyses indicate that the most referenced and highly impactful scientific journals in this field include *Construction and Building Materials*, *Cement and Concrete Research*, and *Materials Today: Proceedings*. These publications have been prominent in publishing findings and advancements in this area.

By adding nanoparticles in the production of cement, it is possible to control several parameters during the hydration process of concrete. Research indicates that incorporating nanoparticles in amounts ≤1% of the cement content can increase the strength of concrete by up to 25%, its diffusion by 75%, and its thermal durability by 30% [7].

In the review by F. Sanchez and K. Sobolev [8], research involving the analysis of cementitious materials and concrete incorporating added nanoparticles has been examined through various spectroscopic characterizations such as NMR, XRD, neutron and X-ray scattering, atomic force microscopy, and others. The authors have demonstrated that nanoparticles, by entering the structure of cement, interact with calcium and aluminum silicate components during the hydration process. In all cases, nanoparticles induce changes in both the surface and internal morphology of cement, thereby influencing its properties. It is known that cement is a crystalline material consisting of a mixture of dicalcium silicate, tricalcium silicate, tricalcium aluminate, tetracalcium alumino ferrite, and lime. The hydration process begins when water is mixed with cement powder, and the additional nanoparticles interact with these components at this stage [9]. While nanoparticles affect the properties of concrete by entering its structure, they do not significantly hinder the hydration process of cement. F. Amor and others [10] have confirmed this by adding zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles to cement up to 3%, showing that while metal oxide nanoparticles enhance the hydraulic and photocatalytic properties of cement, they do not significantly delay the hydration process of the mixture. X-ray analyses have revealed that nanoparticles interact with matrix components such as calcium silicate and aluminum ferrite silicate structures through ion exchange.

In the review paper by N.B. Singh and others [11], it has been demonstrated that the properties of concrete prepared from cement with added nanoparticles such as Al_2O_3, ZrO_2, and Fe_2O_3 are improved. According to analyses, the addition of metal oxide nanoparticles enhances (accelerates) the chemical reactions during the initial hydration period. As a result, the durability properties of concrete are enhanced. The authors attribute this to the involvement of metal oxide nanoparticles in reactions with $Ca(OH)_2$, which leads to the formation of a more compact microstructure.

In another study [12], the authors have shown that the addition of metal oxide nanoparticles to cement increases the amount of calcium silicate hydrates. This leads to an increase in the mechanical properties of concrete (resistance to compression and bending, wear resistance, etc.). Even the addition of TiO_2 nanoparticles to cement induces the formation of a superhydrate layer in concrete. This layer helps to mitigate other photocatalytic reactions, controls energy transfer within the structure, and reduces heat transfer. Moreover, TiO_2 particles sized at 20 nm regulate the hydration period in cement paste and shorten the initial and final value of setting.

In general, the various applications of nanomaterials in concrete, as well as their associated risks to health and the environment, are topics of discussion. Nanomaterials such as nanosilica, nano-TiO_2, carbon nanotubes, iron oxides, polycarboxylates, and nanocellulose can enhance the mechanical and thermal properties of concrete while also improving its durability. This capability may contribute to reduced energy use and overall costs in the concrete industry. However, due to uncertainties and inconsistencies in size, shape, and chemical composition, some nanoscale materials can pose risks to the environment and human health [13]. Therefore, the potential beneficial effects and inadvertent hazards of nanoscale materials on the environment should be carefully considered in the coming years. Additionally, the disposal of construction material residues should also be a matter of concern.

In the review paper by Yonathan R. [7] and Alexander P. [14], it has been concluded that nanoparticles such as SiO_2, Al_2O_3, Fe_2O_3, TiO_2, $CaCO_3$, and clays are highly effective additives for modifying cement products even at low concentrations (≤1%). The addition of these nanoparticles in such quantities has shown to reduce setting time by 1-2 hours, alter spread by 4-75%, increase strength by 5-25%, and enhance heat resistance - residual strength by 0-30%. The exceptional properties highlighted in the research are attributed to the small size and large surface area of nanoparticles, which contribute to their unique reactivity.

Metal Nanoparticles as Additives to Cement

In recent years, the use of nanoparticles in construction materials has garnered significant attention, proving that the nanomodification of cement materials leads to considerable improvements in mechanical properties, compactness, and durability. The incorporation of nano-SiO_2, nanoclay, nano-Al_2O_3, carbon nanotubes, and nanofibers into cement-based materials has been steadily advancing. The effects of modifying cement materials with nanoparticles, such as their hydration, filling, thixotropic effects, and chemical reactivity, influence the quality of the binder materials. Results have shown that fillers like nano-SiO_2, nano-Al_2O_3, nano-limestone, nanoclay, and nano-Fe_2O_3, when applied in optimal doses, yield properties that are significantly enhanced [15].

Metal oxides such as FeO, Fe_2O_3, Al_2O_3, SiO_2, and CaO in cement can interact chemically over an extended period with added TiO_2 nanoparticles. When nano-TiO_2 particles are incorporated into cement paste, the free CaO ions present can easily react with nano-TiO_2 to form $CaTiO_3$ particles. $CaTiO_3$ is a semiconductor and exhibits photocatalytic activity against ultraviolet radiation [16,17]. Most research studies indicate that the band gap energy of $CaTiO_3$ is approximately 3.5 eV [18]. The isoelectric point of $CaTiO_3$ is around pH 3, and based on these energetic values, cement materials with added nano-TiO_2 can be used to create special materials that can partially provide conductivity [19].

In another study [20], the compressive strength of cement paste and concrete mixed with dispersive water containing CuO, ZnO, and Fe_2O_3 nanoparticles was investigated. The authors prepared concrete samples by mixing cement with sand and Cu-Zn-Fe oxide nanoparticles with an average size of 12 nm at a water/cement ratio of 0.4. The method for preparing the mentioned nanoparticles and incorporating them into the concrete structure can be schematically illustrated as follows [Fig. 2].

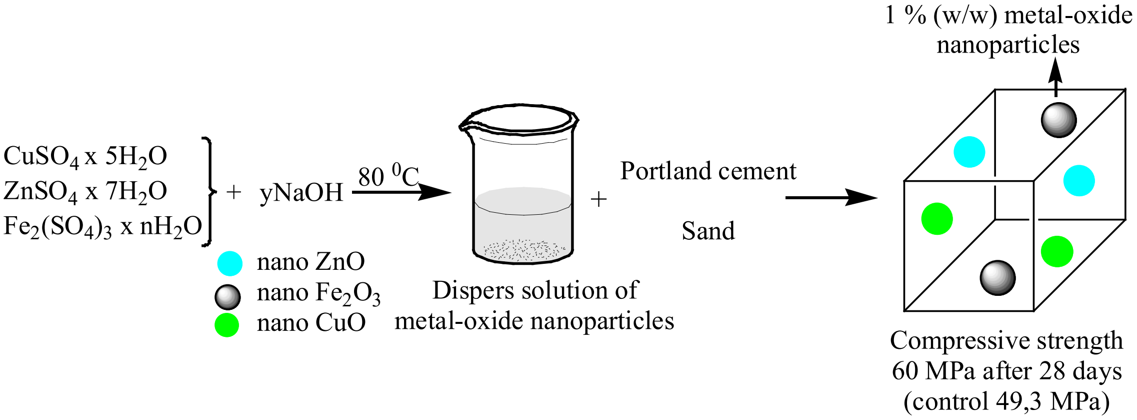

Fig. 2. Schematic representation of the procedure for preparing concrete specimens with ZnO, CuO, and Fe_2O_3 nanoparticles according to M. Kamala [20].

According to the research, Cu-Zn nanoferrite particles occupy certain voids in the concrete, leading to an early hydration process. The increase in compressive strength has proven the effectiveness of using this type of nanoparticle-mixed cement in construction and wellbore zone reinforcement.

Meral O. and colleagues [21] investigated the mechanical properties of concrete by adding 0.5-1.25-2.5% (w/w) nano Fe_2O_3 (60 nm) and nano Al_2O_3 (13 nm) particles, as well as their binary forms, to cement powder. They determined that adding more than 1.25% nanoparticles decreases the compressive strength of the concrete. The compressive strength of the concrete on the 3rd day was 31-32 MPa, which increased to 63-65 MPa after 180 days. When using binary nano-Fe_2O_3/Al_2O_3, the strength increased to 70 MPa. The addition of nano Fe_2O_3, whether alone or in binary form with nano Al_2O_3, only slightly increased the capillary permeability of the concrete.

Roni R. and colleagues [22] studied the crystal structure stability and chemical bonding characteristics of $TiO_2/BaCO_3$-filled composite cement for X-ray shielding using X-ray diffraction and Fourier-transform infrared spectroscopy. In the concrete sample, the Ba–O bond at 714 cm^{-1} and the –OH bond at 2515 cm^{-1} were monitored before and after X-ray exposure. It was shown that these bonds are more durable and continuously interact with the particles in the composite. It was determined that the optimal composition is a 30% (TiO_2 + $BaCO_3$) composite, which shows the highest linear attenuation coefficient of 3.524 cm^{-1} for 60 keV, approximately 3.146 cm^{-1} for 70 keV, and 2.776 cm^{-1} for 80 keV.

In the study [23], the effects of ZrO_2, Fe_3O_4, TiO_2, and Al_2O_3 nanoparticles on cement properties were investigated. A polycarboxylate solution was used as a plasticizer, and the nanoparticles with sizes ranging from 10 to 25 nm constituted 1.5% of the cement. It was determined that with the presence of nano Fe_3O_4, the compressive strength of the concrete reached 119 MPa after 28 days of curing. In comparison, this value was 92.3 MPa without the nanoparticles. It was also found that the addition of nano Fe_3O_4 reduced the penetration of chloride ions into the concrete by up to 40% compared to the control.

In another study [24], a concrete sample was partially modified with TiO_2 nanoparticles and rice husk ash to act as a pozzolanic material. Various compositions of concrete were prepared using 0-5% TiO_2 nanoparticles and a fixed amount of 10% rice husk ash as part of Portland cement. The results indicated that the combination with 3% TiO_2 nanoparticles demonstrated high strength and durability characteristics. It was shown that using more than 3% TiO_2 nanoparticles led to a decrease in strength and durability properties.

The authors [25] prepared Ag° nanoparticle concrete using 0.5% by mass of dextrin in cement with a water/cement ratio of 0.5 [Fig. 3]. They found that dextrin increases the compressive strength of the concrete, while Ag° nanoparticles enhance its microbial resistance. Additionally, dextrin raises the spread diameter of fresh cement paste from 20.5 cm to 28 cm, which is advantageous for outdoor applications such as wellbore zone reinforcement. The polysaccharide increases the compressive strength of the concrete from 48 MPa to 57 MPa, which can be effective against dynamic impacts. Considering the bacterial degradation of concrete, Ag° nanoparticles improve erosional resistance, leading to greater longevity in both construction and oil well applications in contact with formation waters.

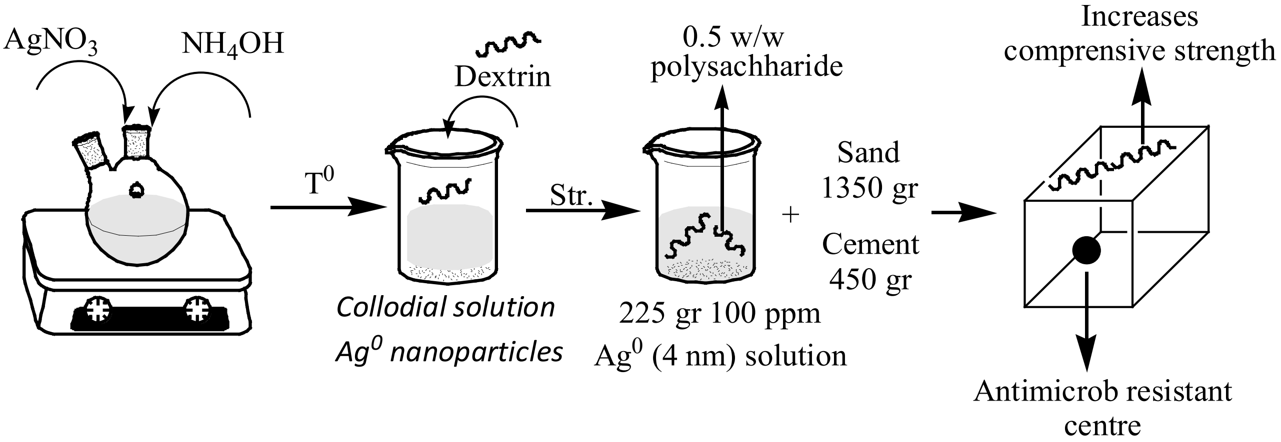

Fig. 3. Schematic representation of the preparation of cement stone modified with dextrin with Ag° nanoparticle E. Konował, etc. [25].

In another study [26], the special role of zinc oxide (ZnO) nanoparticles in improving the properties of cement composites has been emphasized. Zinc oxide nanoparticles possess unique optical, antimicrobial, and photocatalytic properties. These ultrafine nanoparticles exhibit a filler effect and have been shown to influence the hydration reaction in the cement matrix. The application of ZnO nanoparticles provides photocatalytic properties to cement structures. The impact of ZnO nanoparticles on the setting time, microstructure, and strength of cement has been extensively investigated. Research has demonstrated that optimized dosages of these nanoparticles can lead to concretes with high mechanical strength and antimicrobial properties.

The rate and coefficient of water absorption, workability, and hardening time of binary concrete obtained by adding 15 nm TiO_2 nanoparticles to cement in the amounts of 0.5, 1.0, 1.5, and 2.0% by mass were investigated [27]. The results indicated that the use of TiO_2 nanoparticles up to a maximum of 2.0% by mass allows for the production of durable concrete with reduced water permeability. TiO_2

nanoparticles improve the filler effect and significantly increase the pozzolanic action, enhancing the densification of the gel phase. Additionally, the increased content of TiO_2 nanoparticles in the composition has led to reduced workability and setting time of fresh concrete.

The authors [28] have shown that the addition of 1% of 5-10 nm-sized nano TiO_2 particles to the cement composition resulted in a cumulative heat release of 192 J/g over 72 hours. This value was significantly lower compared to the control concrete, which exhibited a 3.23% higher cumulative heat release. It is concluded that nano TiO_2 particles accelerate the hydration of cement. The creation of TiO_2 nanoparticles in a core/shell structure with SiO_2 has shown a better effect on cement hydration and isothermal heat conduction calorimetry in terms of pozzolanic effect.

In reinforced concrete structures, the steel-concrete matrix is highly susceptible to corrosion and degradation under the influence of environmental ions (e.g., chloride and sulfate ions). Authors [29] have prepared concrete samples where the addition of certain metal oxide nanoparticles has decreased the ion permeability of concrete while increasing its strength and durability. The addition of metal oxide nanoparticles accelerates chemical reactions during initial hydration, resulting in stronger cement composites. These nanoparticles react with $Ca(OH)_2$ to enhance the formation of calcium silicate hydrate (C-S-H), leading to a more compact microstructure. For example, Zhang and Li [30] demonstrated that adding 1% (by weight of binder) of 15 nm-sized TiO_2 to concrete improves its microstructure and increases resistance to chloride penetration by 31%.

When combined with conventional construction materials, nanoparticles can endow new materials with specific properties suitable for the construction of ultra-high, long-span, or intelligent infrastructure systems. There is potential for TiO_2 nanoparticles, which are part of white cement, to possess photocatalytic properties that can preserve the aesthetic characteristics of architectural and decorative concrete over time [31]. White cement containing photocatalytic, self-cleaning nanoparticles has been used in the construction of the modernist "Misericordia Immersion" church in Romada. Coatings of 15 nm-sized TiO_2 particles have been applied to glass windows for the photocatalytic degradation of dirt particles adhered to the glass [32].

Nano-MgO is a newly researched reactive nanocomponent in cement materials. Due to its soft expansion upon contact with water, Nano-MgO offers significant advantages in cement material production by compensating for shrinkage [33]. Reza et al. have studied the effect of nano-MgO on the microstructure and compressive strength of cement composites [34]. The results have shown that the compressive strength durability has increased by 103% and 80% respectively, after 7 and 28 days in samples containing 1% nano-MgO, while the flexural strength has correspondingly increased by 95% and 70%.

Heikal and others [35] have demonstrated that the application of nano-Al_2O_3 at a 1% mass ratio in cement paste accelerates the hydration of the cement mass, acts as a nano-filler, and provides better thermal resistance up to 1000°C compared to other pastes.

There are numerous studies in the literature on how the physical and mechanical properties of cement change with the addition of TiO_2 nanoparticles. One study notes that nano-TiO_2 can accelerate the hydration of Portland cement [36], while another shows that it increases the compressive and flexural strength of cement stone [37]. For pavement applications, the abrasion resistance of concrete with added nano-TiO_2 and nano-SiO_2 particles has been experimentally confirmed [38]. The abrasion resistance of concrete with nano-TiO_2 was more effective than that of concrete with the same amount of nano-SiO_2. Concrete with nano-TiO_2 has been proven to be very effective in self-cleaning and environmental decontamination. This is because nano-TiO_2 influences the photocatalytic degradation of pollutants [39].

It is known that the clean surface of TiO_2, with the involvement of sunlight, allows for the oxidation of harmful NO_x gases into nitrates, thus removing them from the atmosphere. Photocatalytic concrete blocks for road surfaces have been found effective in neutralizing NO_x gases [40]. Surface reactions have been extensively studied using X-ray photoelectron and Raman spectroscopy [41], and nano-TiO_2-based 'self-cleaning' concrete products have been developed for use on building facades and concrete road surfaces in Europe and Japan.

It has been determined that the fatigue properties of concrete with added nano-TiO_2 particles significantly improve during bending, and this increases its sensitivity to stress changes. Concrete with nano-TiO_2 (1.0%) has been experimentally proven to exhibit better flexural fatigue properties than concrete with polypropylene fibers, which are widely used for road surfaces [42].

The photocatalytic properties of nano-TiO_2 can be efficiently used to clean certain environmental pollutants under ultraviolet radiation. Thus, cement-based coatings, including nano-TiO_2, are more suitable for use on the exterior surfaces of buildings. Due to the high agglomeration of TiO_2 nanoparticles in the cement environment, their photocatalytic activity is significantly reduced [43]. The effective prevention of external agglomerations can be achieved by using TiO_2 nanoparticles in a dispersed form in lime-saturated solution within cement mixtures. The microstructural properties of concrete with nano-Ti_2O_3 additives have been studied by Feng and others [44], and it has been determined that nano-Ti_2O_3 in the cement matrix facilitates the formation of a homogeneous dense calcium silicate hydrate gel. Additionally, nano-Ti_2O_3 particles ensure the continuous distribution of hydration throughout the cement matrix.

In another study [45], the application of nano-Ti_2O_3 improved the pore structure, increased the density of the concrete by acting as filler, and activated the hydration of the cement while reducing the size of calcium hydroxide crystals. When the amount of nanoparticles exceeded 4%, the formation of $Ca(OH)_2$ crystals was limited due to restricted growth space. As a result, the microstructure became more porous, negatively affecting the compressive strength of the cement matrix.

Farzadnia [46] determined that concrete with nano-TiO_2 additives exhibited higher compressive strength, brittleness, and gas permeability up to a temperature of 600°C compared to the control sample. Due to the nanoparticles, the mass loss decreased, and although the average mass loss of the control concrete was 13.5% up to 650°C, for concrete with 3% - 4% nano-TiO_2, the mass loss was 16.7% and 17.5%, respectively.

Various researchers have studied the properties of concrete with two or more nanoparticles. Zhang [47] investigated the properties of TiO_2–graphene composites added to cement at mass ratios of 0.01%, 0.03%, and 0.05%. Compared to the control concrete, compressive strength increased by 26.6%, and flexural strength increased by 11.3%. By using filler at a 0.03% mass ratio, the capillary sorption coefficient decreased by 1.2 times, and a 68.7% reduction in chloride penetration was observed.

Guo and others [48] determined that the addition of a 0.5% TiO_2-graphene complex to a polymer epoxy matrix reduced the capillary sorption capacity of cement stone by 52.22% and the chloride diffusion rate by 77.43%.

TiO_2, with its self-cleaning and antibacterial properties, and SiO_2, which forms significant mechanical properties, have been studied for their combined use in producing concrete samples. The negative charges on the surface of the TiO_2–SiO_2 nanocomposite can be evenly distributed in the concrete mixture, significantly improving compressive and flexural strength, as well as dynamic compressive capacity [49]. Another study demonstrated that using 3.0% by mass of reactive powder TiO_2–SiO_2 increased the compressive strength of concrete by 12.26%, and using 5% increased the flexural strength by 87% [50].

Al_2O_3 nanoparticles are very effective in increasing the elastic modulus of cement mortar. For instance, the elastic modulus of cement mortar with 5% 150 nm Al_2O_3 nanoparticles increased by 28% over 143 days [51]. A proper mixing procedure was selected to ensure the adhesion of Al_2O_3 nanoparticles to the sand surfaces. Effective compaction with Al_2O_3 nanoparticles resulted in a significant increase in the elastic modulus of the paste. However, when the nanoaluminum content exceeded 5%, the agglomeration of nanoparticles led to inefficient compaction, resulting in a decrease in the elastic modulus of the mortars.

The effect of adding synthetic nano ZrO_2 particle powder to cement on the strength of Portland cement paste has been studied [52]. The addition of nano-ZrO_2 powder to cement resulted in a decrease in porosity and permeability, an increase in compressive strength, and an improvement in the microstructure of the cement paste. Both pore filling and overlapping were identified as possible enhancement mechanisms.

Han and others [53] investigated the change in resistance during the compression of cement mass containing two types of TiO_2 nanoparticles (i.e., anatase and rutile-based) and nanocarbon fiber. It was observed that cement paste with anatase-based nano-TiO_2 (i.e., polymorphic TiO_2) exhibited pressure-sensitive characteristics, whereas paste with rutile-based nano-TiO_2 did not. The cement paste containing carbon fiber had the best pressure sensitivity at the lowest resistance. The rate of resistance decrease was 7-10% for nano-TiO_2 (anatase) paste and 17-35% for carbon fiber paste.

Results of zeta potential and particle size distribution indicated that high agglomeration of nano-TiO_2 occurs in the cement paste with the usual mixture. A proper mixing scheme of dispersing nano-TiO_2 in saturated lime water by ultrasonication and subsequently adding the resulting suspension to cement powder not only leads to the correct distribution of nano-TiO_2 in the cement but also enhances the photocatalytic properties of the nanoparticles in the cement under ultraviolet irradiation due to the formation of $CaTiO_3$ [54].

To better understand the effect of nano-TiO_2 on the properties of cement-based materials, the hydration process, the increase in compressive strength, and the drying and pressing of cement-based materials with the addition of 2 nm nano-TiO_2 were investigated. The results showed that nano-TiO_2 accelerates the hydration of cement and the cleaning of pores, increasing the compressive strength of the cement paste: 5% by mass of nano-TiO_2 accelerates the hydration process of cement by 2 hours and reduces the most probable pore size by up to 54.4%. For comparative study, 30 nm SiO_2 was also used. The results indicated that [55] reducing the wetting angle and improving the pore structure with the addition of nano-TiO_2 reduced water loss with hardened cement paste, resulting in pressing comparable to that of the 1-month control sample.

Concrete Samples with Magnetite Nanoparticles and İmproved Properties

As mentioned, the addition of iron oxide nanoparticles to concrete results in improvements in its properties, particularly in durability. In the study [56], the mechanical properties of Portland cement were investigated by adding magnetite Fe_3O_4 colloidal solution at ratios of 0.05%, 0.1%, and 0.3%. It was shown that the compressive strength of magnetite nanoparticle cement paste increases at all ages of hydration. For instance, the compressive strength increases from 240 $gH/kg{\bullet}cm^{-2}$ to 850 over 100 days. According to XRD results, magnetite nanoparticles slightly increase the crystallinity of the concrete. This is reflected in the thermal behavior observed by DSC, where the main decomposition starts at 490°C, whereas in pure cement concrete, this process is observed at a relatively lower temperature.

Authors [57] determined that when the ferrite content in cement for well cementing is high, the concrete possesses greater hardness. Based on petrographic results, the lithological structure of high-ferrite oil well cement is evenly distributed, and the particle size is moderate. Additionally, according to XRD and DTG analyses, the hydration products in the cement paste are more tightly bonded, resulting in a more compact structure. Studies were conducted by adding iron slag to cement in amounts ranging from 2.3% to 4.2% of the total mass. It was shown that the elastic modulus becomes optimal when the iron slag content is 3.4% over 3 and 7 days.

In another study [58], thermal treatment of cement powder containing 3% (by mass) of magnetite nanoparticles with sizes ranging from 50 to 100 nm was conducted at temperatures ranging from 200 to 800°C. The prepared magnetite nanoparticle concrete exhibited a 10-11% increase in tensile strength after thermal treatment at 200°C. The mechanical properties after heating to 300°C were comparable to those of untreated samples. Compressive strength also increased by 13-14% after treatment at 300°C. The authors demonstrated that Fe_3O_4 magnetite nanoparticles can preserve the integrity of the concrete matrix during thermal perforation.

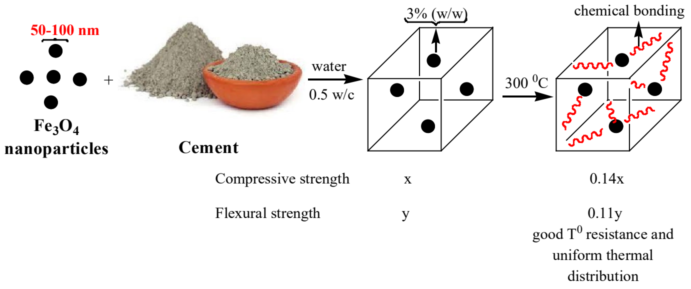

Fig. 4. According to Pawel Sikora [58], indicators of compressive and flexural strength of concrete stone due to Fe_3O_4 nanoparticles.

In studies [59], it has been observed that without metal nanoparticles, the mechanical properties of polymer-modified cementitious mortar can also be enhanced. Concrete prepared by adding butadiene-styrene emulsion (1-8% by mass) has been extensively researched for water absorption, compressive/flexural strength, spreadability, splitting tensile strength, and surface morphology. It has been determined that the use of 1% SBR increases compressive strength from 52.29 MPa to 65.58 MPa over 28 days. Splitting tensile strength also increases from 3.58 MPa to 4.76 MPa when compared to the control. The incorporation of long-chain polymer macromolecules into the visible cement particles connects them. Chemical interaction of calcium silicate structures with copolymer compactifies individual concrete fragments. As a result, the durability and elasticity of the concrete sample are strengthened. As seen, as the emulsion content increases, the material becomes more amorphous, thereby increasing elasticity. When 1% polymer is used, compressive strength reaches its maximum.

The authors [60] have demonstrated that adding 1% nano Fe_3O_4 to the concrete composition exhibits long-term high electrochemical stability. Even after exposing the concrete sample to chlorine and SO_2 gases for 300 days, the indicators remained unchanged. Additionally, after 28 days, concrete absorption decreased while the elastic modulus and axial compressive strength increased. Magnetite nanoparticles prevent micro-cracks in the cement matrix, contributing to its long-term durability, as evidenced by SEM micrographs by the authors.

In another study [61], the influence of magnetite nanoparticles on the durability of concrete under varying temperatures was investigated. The authors demonstrated that adding 1% nano Fe_3O_4 to cement limits its mass loss to less than 2% at 800°C. The maximum flexural strength occurs at 100°C, reaching up to 13 MPa, and decreases thereafter, reaching 0.8-1.0 MPa at 800°C. Compressive strength peaks at 75-80 MPa between 100-200°C but decreases to 10 MPa at 800°C. These findings indicate that magnetite nanoparticles not only enhance the mechanical properties of cement concrete but also increase its thermal stability. Moreover, they help preserve the integrity of concrete surfaces by preventing cracking at high temperatures, as evidenced in SEM studies conducted by the authors.

In another study [62], 1-2% nano Fe_2O_3 particles were added to cement powder (mixing and preparation temperature 300-500°C) with a water-cement ratio of 0.35. The prepared concretes were heated up to 1000°C, held for 3 hours, and their mechanical properties were studied. The processes involved in the synthesis of magnetite nanoparticles and the preparation of concrete can be schematically represented as shown below [Fig. 5].

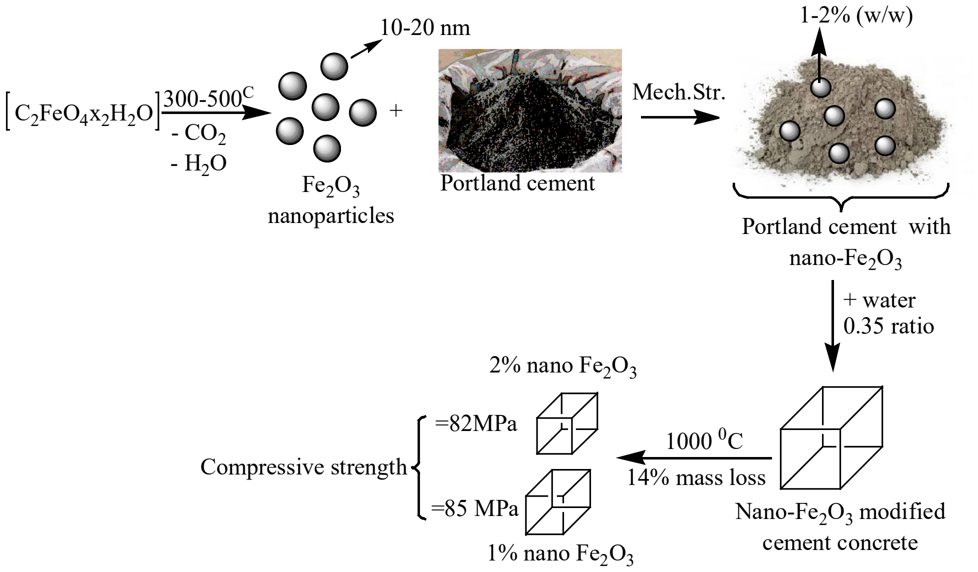

Fig. 5. Preparation of magnetite nanoparticle concrete derived from organic iron salts and evaluation of its compressive strength [62].

The author investigated the increase in chemically bonded water in the composition due to the presence of nano Fe_2O_3. This is explained by the nanoparticles acting as nucleation sites during the hydration process, resulting in the formation of more hydrated Ca-Si-hydrates. The compressive strength values of the concrete after different thermal treatments with various amounts of added magnetite nanoparticles can be seen in [Fig. 6].

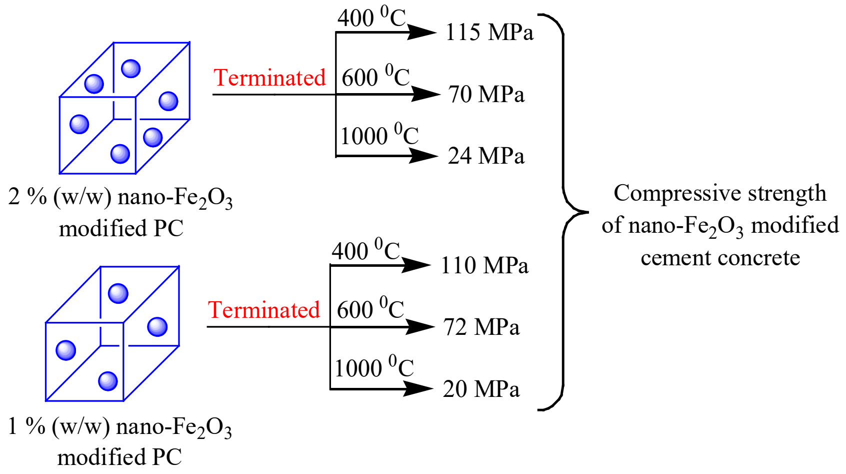

Fig. 6. Dependence of compressive strength values on temperature treatment for concrete filled with 1% and 2% nano Fe_2O_3.

As can be seen, the inclusion of nano Fe_2O_3 in the cement structure enhances its durability. Nanoparticles regulate the hydration process by forming a more homogeneous and compact matrix during hydration. Following the other studies by Hui Li [63], the sensitivity to pressure of cement with added nano Fe_2O_3 was investigated. It was found that nano Fe_2O_3 does not reduce the sensitivity of the cement stone. It was shown that when the concrete contains 3-5% nano Fe_2O_3, its volume resistance decreases by 20-45% (stress-sensing sensitivity). Additionally, as the load is applied to the concrete, the electrical resistance of the sample decreases. The authors explain this by the convergence of nano-Fe_2O_3 particles during concrete compression, creating a tunneling effect that intensifies the current flow. Such materials are significant for load detection, evaluation, and the creation of self-diagnostic materials.

Nano-Fe_2O_3 particles not only enhance the durability of the concrete but also improve its fire resistance. In the study [64], $(CH_3COO)_2Fe$ was thermally decomposed at 275°C, 600°C, and 800°C [Fig. 7], and then added to the cement composition (1%, 2%, 3%) to investigate the mass loss.

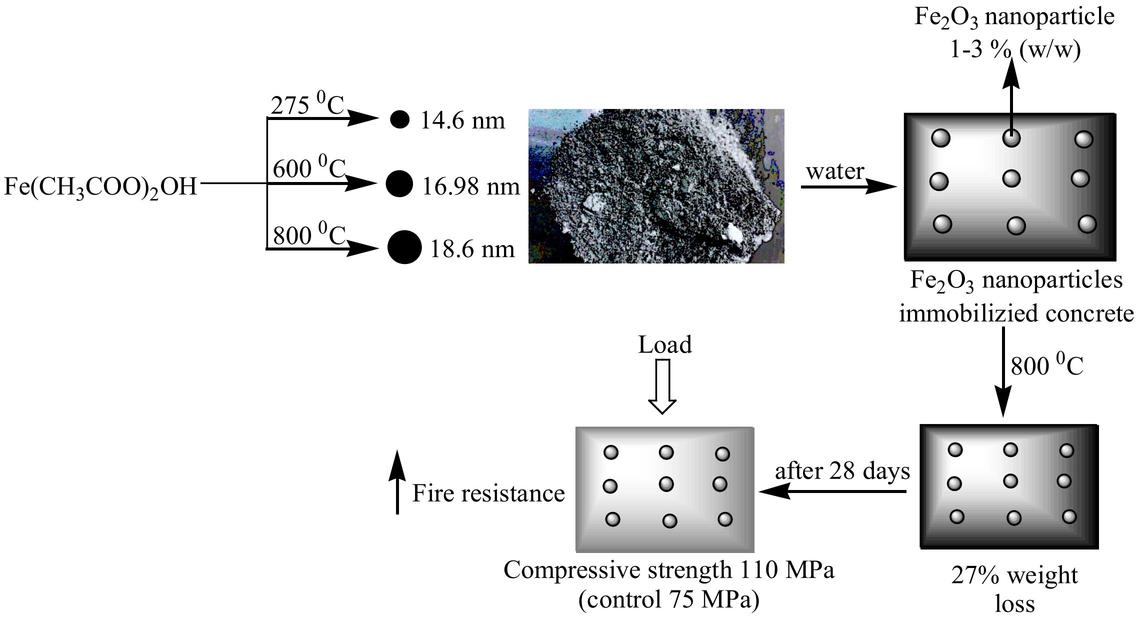

Fig. 7. Preparation of fire-resistant concrete by adding iron-acetate-sourced Fe_2O_3 nanoparticles to cement powder, mass loss, and durability changes [64].

It was determined that cement paste incorporated with 1% nano-Fe_2O_3 shows the lowest weight loss up to 800°C. As the amount of nano-Fe_2O_3 increases to 27%, the weight loss also increases. The authors attribute this to the effect of nano-Fe_2O_3, enhancing the formation of hydration products that precipitate in the open pores with low free water content. Cement paste containing 1% nano-Fe_2O_3, when treated at 400°C, increases in compressive strength from 75 MPa to 110 MPa compared to the control.

The authors [65] studied the physical and chemical properties by adding Fe_2O_3 and Fe_3O_4 particles smaller than 5µm, as well as 50 nm NiO nanoparticles, in amounts ranging from 0.5% to 3.0% (w/w) to cement. They showed that the compressive strength of concrete with magnetite nanoparticles can increase by up to 47.6% after 7 days. After 28 days, this increase is 11.9% compared to the control. As the amount of nanoparticles increases, durability also increases. Although nanoparticles increase the density of the cement, they have a slight effect on the water absorption capacity of the concrete. For example, 3% nano-Fe_3O_4 only slightly changes the absorption capacity, resulting in well-crystallized microstructures, with nanoparticles coherently associated with cement particles and well-compacted.

In this study [66], green magnetite nanoparticles (Fe_3O_4) were synthesized using plant-based raw materials. These nanoparticles were applied as electrically conductive fillers in cement mortars formed by replacing sand with fine aggregates from two types of industrial waste: steel slag and mill scale. The study examined the effects of water/cement ratio, the content of green conductive fillers, and industrial waste on the electrical resistivity and compressive strength of the prepared mortars. The results indicated that increasing the content of conductive fillers decreased electrical resistivity and increased compressive strength. According to response surface analysis results, the optimal electrical resistivity of the smart cement-steel slag mortars was found to be 8.83 Ohm·m. The authors also developed a mathematical correlation between electrical resistivity and compressive strength.

Khoshakhlagh and colleagues [67] investigated the hydration heat of cement pastes modified with nano-Fe_2O_3 over 70 hours. They conducted measurements by adding nano-Fe_2O_3 to the cement at proportions of 1%, 2%, 3%, 4%, and 5% by weight. The results indicated that adding up to 4% by weight of Fe_2O_3 nanoparticles positively influenced the hydration process, accelerating it and yielding favorable results in calorimetry tests.

Research has shown that nano-Fe_2O_3 can enhance the compressive and flexural strength of concrete while also providing self-healing capabilities, making it invaluable for real-time structural health monitoring and the construction of smart structures [68].

Nazari and colleagues [69] investigated the performance of concrete with partial modification of cement using Fe_2O_3 nanoparticles. In their experiment, Fe_2O_3 nanoparticles with an average diameter of 15 nm were used in proportions of 0.5%, 1.0%, 1.5%, and 2.0% by weight of the cement. The results indicated that as the content of Fe_2O_3 nanoparticles increased, the performance of the concrete decreased.

Cement Stones Modified with Polymer-Metal Nanoparticles

Sometimes, polymer-nanoparticle composites are highlighted to regulate both the mechanical and rheological properties of prepared concrete samples. While the polymer regulates the elasticity and hydration processes of the concrete, the metal nanoparticles enhance parameters such as compressive and flexural strength. In the study [70], the surface of the cement stone was investigated by using curana fiber stabilized with polyaniline and magnetite nanoparticles as a binder. They showed that plant fiber increases the adhesive properties of the cement. Polyaniline-modified fiber ensures a stable and durable chemical bond between the cement components and nanoparticles. The inclusion of fiber and polymer in the concrete structure makes it lighter, while magnetite nanoparticles enable electromagnetic properties in the concrete. Additionally, the hydrophobic polymer prevents the sample from getting wet, limiting the formation of cracks.

There are numerous studies that demonstrate the improvement in durability by adding polymer-nanoparticle emulsions to cement. In the study [71], a polymer nanocomposite latex with butadiene-C nanotubes was synthesized. By adding the obtained carbon nanotube latex composite to the cement (specifically up to 1-4% of the volume of water), they observed that the compressive strength of the concrete increased from 18 MPa to 19.5 MPa, and the flexural strength increased from 16.5 MPa to 17.4 MPa. The authors explained that the adhesive capability of the polymer latex ensures the mutual adhesion of cement particles. The additive effectively controls liquid loss for hydrostatic pressure and hydration, while also increasing surface tension in the cement paste during fresh hydration, preventing early shrinkage and breakages. As a result, the modulus of elasticity increased by 75%, and the flexural strength increased by 48%.

In the present study, the nature of the chemical interactions formed in the composition by the simultaneous inclusion of poly-N-vinylpyrrolidone (PVPr) and magnetite nanoparticles into the cement structure was studied [72]. For this purpose, cement samples were prepared by adding 1% PVPr and 1-2% magnetite nanoparticles to tamponade cement with a water/cement ratio of 0.5 (by dry weight of the cement). The FTIR and XRD spectra of the obtained concrete samples were comparatively analyzed. It is known that concrete made from cement is a material with a hard structure, mainly consisting of calcium and aluminum silicates, constructed with ionic bonds. For comparison, the XRD spectra of hydrated cement, PVPr concrete, and PVPr/Fe_3O_4 concrete stones were obtained. It is known that the XRD spectrum of concrete made from cement [73] shows specific peaks for di- and tricalcium silicates, as well as calcium-aluminum silicates, at $2\theta = (26.58^\circ)$, (29.55°), (32.49°), (34.12°), (41.32°), (47.23°), (50.68°), and (51.87°). Concrete made with 1% PVPr shows slightly different XRD patterns compared to its predecessor. PVPr is an amorphous substance and, being 1% in composition, does not form distinct peaks in the X-ray spectrum [74]. However, since the polymer interacts with Ca-Al silicates in the cement, it causes some peaks to decrease in intensity or shift at certain 2θ values. Such shifts are particularly noticeable at $2\theta = (39.32^\circ)$, (43.42°), and (54.62°). The formation of a secondary line at $2\theta = (56\text{-}58^\circ)$ proves the immobilization of PVPr in the cement structure. It was found that increasing the amount of magnetite nanoparticles in the concrete composition leads to the clarification of characteristic peaks in the X-ray spectrum and a certain increase in their intensity. Additionally, the harder crystal structure of magnetite nanoparticles further strengthens the X-ray spectrum of the concrete. It is known that iron atoms in magnetite nanoparticles are not in an ionic form (charged) but are composed of particles with sizes ranging from 30-45 nm. The observation of characteristic peaks in 2θ values, typical for magnetite nanoparticles, indicates that the nanoparticles have not undergone size changes in the concrete.

According to FTIR results, the inclusion of PVPr macromolecules in the concrete composition leads to the observation of some peaks specific to the polymer in certain regions. Additionally, the chemical interaction of functional groups in PVPr with elements in the cement causes chemical shifts in some regions characteristic of concrete. It is known that in the FTIR spectrum, PVPr exhibits absorption bands at 1646 and 3450 cm^{-1} corresponding to the >C=O and -OH groups, respectively [75]. Additionally, bands are observed at 2950 cm^{-1} for the asymmetric stretching of CH_2 in the pyrrolidone ring, at 2922 cm^{-1} for CH_2 in the polymer chain, and at 1286 cm^{-1} for the vibrational stretching of CH_2 attached to C-N [76]. Although the FTIR spectrum of PVPr concrete does not show distinctly new peaks with different intensities, absorption bands with slight modifications are observed.

According to the FTIR results of PVPr concrete, the polymer is embedded in the pores of the concrete and actively interacts chemically with the metal silicates. The carbonyl groups in PVPr are involved in the main interaction. Specifically, the absorption band at 1646 cm^{-1} characteristic of the carbonyl group in pure PVPr shifts chemically to the 1653 cm^{-1} region in the concrete. This, in turn, causes slight chemical shifts in some bands characteristic of silicates in the concrete.

Based on the results of FTIR spectroscopy, XRD, and TGA investigations, the chemical bond formed between the cement particles and the polymer chains can be schematically represented as follows [77]:

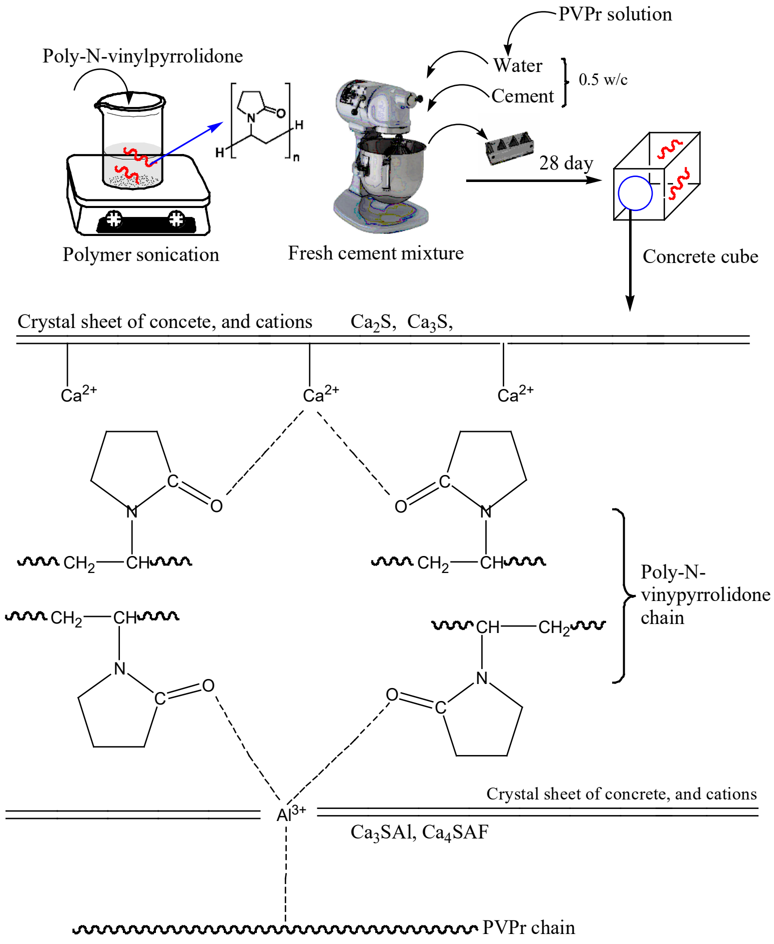

Fig. 8. Schematic representation of the preparation of PVPr-modified concrete and the chemical interaction between particles.

All this proves that PVPr macromolecules are immobilized in the pores of concrete with silicates, and similar results are found in other studies [78]. The inclusion of PVPr-coated magnetite nanoparticles in the concrete results in the formation of oxide-related absorption bands in the FTIR spectrum [79]. Specifically, the characteristic absorption band for magnetite nanoparticles is observed at 541 cm^{-1}, and the carbonyl group peak of PVPr, which is actively chemically interacting with Fe_3O_4 nanoparticles, shifts to the 1635 cm^{-1} region. In other regions, the characteristic absorption peaks of silicates in cement show only slight chemical shifts. This indicates that magnetite nanoparticles are more actively chemically bonded with PVPr in the concrete structure, while they are relatively passively bonded with cement components. This can be explained by the faster interaction of Ca and

Al silicates with water molecules and PVPr during the cement hydration phase. Additionally, considering that magnetite nanoparticles are mixed with cement powder in a complex with PVPr macromolecules, it is understandable that iron oxide molecules are more concentrated around the polymer.

Concrete Structures with Core/Shell SiO_2/Me Nanoparticles

In some studies, the combined addition of silicon oxide and metal nanoparticles to cement has resulted in superior properties. For example, in the study [80], the mechanical properties were investigated by adding nano Fe_3O_4 (30 nm) and nano SiO_2 (15-20 nm) to the cement composition. The authors showed that as the amount of nano-Fe_3O_4 increases, compressive strength increases by 20% and 3.7% over 7 and 28 days, respectively. Additionally, flexural strength increases by 30% and 23%. Although the nanoparticles fill the pores in the cement stone, they act as activators in the hydration process. When nano-Fe_2O_3 is added to cement together with nano-SiO_2 (9.0 g of nano-SiO_2, 13.5 g of nano-Fe_2O_3 per 768 cm^3 of cement), compressive and flexural strength increase by up to 27-22%. The authors demonstrated that nanoparticles evenly distributed within the cement paste act as nuclei and form conglomerations by gathering cement particles around them (due to their high surface energy) during the hydration process. The chemical bond between the nuclei and the transmitting substances strengthens the concrete.

In the study [81], both nano-SiO_2 and nano-Al_2O_3 were added separately and together, and the stability, pore structure, flexural strength, and other properties of $MgCl_2$-modified cement stone under 60 kPa pressure and 60% humidity were investigated. The authors showed that at low pressure, the cement stone gets damaged, and erosion products like $Mg(OH)_2$, $Ca_2Al(OH)_6Cl•2H_2O$, and $Mg_2(OH)_3Cl•4H_2O$ form in the presence of free $MgCl_2$. The nano-modification reduced the number of harmful pores larger than 50 nm and blocked the eroded $Ca(OH)_2$ in the samples.

The authors [82] created 50-100 nm-sized core/shell Fe_3O_4/SiO_2 structures by treating magnetite nanoparticles with tetraethyl orthosilicate. They prepared a dispersed solution of nano-Fe_3O_4/SiO_2 particles and cement paste (0.5 w/c) and investigated Young's modulus. They determined that concrete samples containing 1-5% nano Fe_3O_4/SiO_2 particles had improved elasticity modulus. Although deterioration in mechanical properties was observed at 1% nano Fe_3O_4/SiO_2, Young's modulus was 0.056 and 0.013 GPa at 4-5% nano Fe_3O_4/SiO_2, respectively. Local agglomerates formed due to the uneven distribution of nanoparticles in the cement matrix, increasing the porosity of the cement stone. The chemical explanation was attributed to the increased amount of Ca-Si hydrate due to the pozzolanic reaction of the nanoparticles with $Ca(OH)_2$.

Cement Mortars Treated with Metal Salts

In some studies, the addition of not only metal nanoparticles but also nitrates, sulfates, and organic salts of certain metals to cement has been shown to enhance both the initial and post-hardening mechanical properties of the cement mixture. The addition of metal salts to cement affects not only the mechanical properties but also the initial hydration process, allowing control over the hardening process. In the study [83], the effects of certain metal nitrates on the early hydration process and the properties of hardened cement pastes were investigated. Heavy metal ion nitrate salts (lead, cadmium, and nickel) were added to hydrated cement composites at 1%-5% of the cement weight, and their impact on mechanical properties was comprehensively evaluated. It was determined that these salts affect the rate of cement hydration, with Pb compounds significantly slowing down the hydration process. As a result, compressive strength is very low during rapid hardening, and some properties weaken compared to the control.

In another study [84], the effects of chloride salts of alkali, alkaline earth, and transition metals on the hydration and mechanical properties of iron-rich calcium aluminate cement were investigated. The addition of alkali metal salts accelerates the hardening time of cement in the order of Li>Na>K>Rb>Cs, while the long-term strength deteriorates as the ion radius of the metals decreases. The authors explained this by the formation of tetrahedral symmetry by lithium cations. The effect of alkaline earth metal chlorides was related to their concentrations. 0.1% salt solutions slightly delayed the hardening time of the cement, while higher concentrations caused a sudden acceleration of hardening. Transition metal chlorides delayed hardening in the order of Zn>Cu>Mn>Co. The authors attributed the delay effect to the deposition of a protective amorphous gel on the particle surfaces, which inhibits the growth of crystalline hydration products and blocks hydrolysis.

The X-ray, hardening time, and compressive strength of high-Al cement mixtures were investigated using Cr, Cd, Pb, Zn, and Mg salts at various concentrations [85]. The addition of 100-15000 ppm to cement proved the effectiveness of metal salts in converting metastable hydrates to stable hydrates.

In another study [86], the effect of mixtures consisting of alkali slag activated with various concentrations of Cl^- ion salt solutions (NaCl, $CaCl_2$, and $MgCl_2$) on the mechanical strength of cement was investigated. The results showed that numerous 0.01-0.1 μm micro-pores form in the sample with high concentrations of Na^+ replacing Ca-Al-silicate, reducing the cement's binding strength by 3.2-25.0%. Ca^{2+}, on the other hand, helps to form dense internal structures and high-strength fillings. Magnesium ions adsorb $Ca(OH)_2$, reducing alkalinity, significantly affecting the disintegration of slags, but accelerating the dissolution of desulfated gypsum.

Magnesium-phosphate cement was prepared using magnesium oxide, ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and potassium dihydrogen phosphate (KH_2PO_4) salts [79]. As a result, the cement exhibited high strength and hydration temperature. Additionally, the addition of sodium orthophosphate significantly improved the mechanical properties of the cement and extended its hardening time.

The authors [87] investigated the effects of Ba, Cu, Ni, Zn, Cr, Pb, and Cd metal salts on Portland cement with a 0.4 water/cement ratio at 0.1-1.0% by mass. They showed that low doses of metal nitrate additives reduce the hydration of the cement by up to 50% and simultaneously decrease its porosity.

Tests and permeability tests were conducted on cement-bentonite mixtures with various hardening times using K_2SO_4 solutions [88]. The results showed that permeability negatively affects the hydraulic properties of the cement-bentonite mixture, depending on the sulfate concentration and mixture composition. It is also important to select a very low-permeability mixture to limit the negative effects of SO_4^{2-} interaction on hydraulic properties. It was determined that although the sorption of K^+ ions by cement-bentonite is significant, hardening remains stable.

Some studies on the application of cement slurries filled with metal nanoparticles in the oil and gas industry have been conducted. It has been shown that using hematite [89] and perlite [90] in nanoparticle form, compared to larger sizes, does not cause problems such as weight increase and settling. This positively affects the thermal conductivity of the cement paste, increasing its stability.

Based on the findings of this study[91], to more precisely determine the chemical role of magnetite nanoparticles in the structure, cement paste was also prepared in the presence of iron salts, and the X-ray spectra were compared. It has been determined that the addition of iron ions to the cement paste significantly affects its hydration and hardening process. Metal ions hinder the hydration of Ca and Al silicates in the structure during the hardening process of concrete, leading to the formation of a brittle structure. X-ray analyses suggest that a 1% PVPr addition does not affect the crystal structure of concrete. On the contrary, it ensures long-distance bonding by creating coordination links between the Ca and Al silicates in the cement. Incorporating magnetite nanoparticles with the polymer into the concrete further hardens the structure and fills some voids in the pores. Moreover, PVPr chains function as bridges between cement particles and magnetite nanoparticles in the concrete. The role of magnetite nanoparticles in such link functions has been observed in various studies. Despite the iron ions being present at only 0.1% of the cement mass, their active interaction with silicates is evidenced by the characteristic lines in the spectrum. The active chemical interaction of iron ions with silicates causes a sharp decrease in the intensity peak at 964 cm^{-1}, characteristic of Si-O. On the other hand, the passive presence of PVPr results in the disappearance of the broad band characteristic of -OH groups in the 3400-3500 cm^{-1} region.

Comparative analysis of FTIR spectra indicates that the addition of PVPr-containing magnetite nanoparticles to the solvent used for preparing cement paste does not hinder its hydration process. The homogeneous distribution of polymers and iron oxides in the structure ensures that PVPr-silicate and PVPr/Fe_3O_4/silicate bonds are distributed throughout the entire volume and surface, rather than being localized. This ensures that the mechanical properties are maintained uniformly throughout the concrete. Research has shown that the mechanical properties of polymer/cement systems are strengthened due to macromolecular chains [92].

In another study, the authors investigated the mass changes of concrete filled with 1–2% polyacrylamide/Fe_3O_4 nanoparticles (by cement mass) in seawater and formation water. Additionally, the IR and X-ray characteristics of the prepared samples were analyzed to determine the chemical state of the polymer and nanoparticles in the structure. It is known that the composition of concrete during operation is adjusted based on environmental conditions and the place of application. In the study, concrete samples were prepared by adding magnetite nanoparticles synthesized in a polyacrylamide medium to Portland cement. After 28 days of complete hardening, the mass changes in the hardened stones were studied in the Caspian Sea and formation water and compared with the control concrete. It has been determined that both the control concrete and the concrete with 2% (w/w) PAA/Fe_3O_4 nanoparticles underwent the same degree of adsorption process over 10 days. The concrete with 1% PAA/Fe_3O_4 nanoparticles experienced 4-4.5% more mass increase, with the sample showing up to 15% adsorptive mass change over 40 days. As seen, the penetration of ions is limited in the 2% PAA/Fe_3O_4 nanoparticle concrete, resulting in even smaller mass changes compared to the control concrete. Overall, it is visible that after 40 days, the mass increase stabilizes in all cases. It is assumed that the higher adsorption in the 1% PAA/Fe_3O_4 nanoparticle concrete sample is due to the magnetite particles. PAA macromolecules ensure the long-term stability of the magnetite nanoparticles' size. As the PAA-coated magnetite nanoparticles are dispersed at 1% (by weight), they allow for the formation of pores that enable water molecules to penetrate the inner layers. As the concentration of magnetite nanoparticles increases, the concrete surface becomes hydrophobic, making it difficult for salt ions and water molecules to penetrate. Since adsorption occurs only on the surface, the iron oxides protect the penetration of hydrated ions into the concrete.

Observations made in formation water, compared to seawater, resulted in relatively different outcomes. The control concrete sample showed a 9-9.2% mass increase over 40 days in formation water. In the concrete modified with magnetite nanoparticles and PAA, the adsorption of formation water increased with the quantity of nanoparticles. However, in this case, the concrete filled with 1% Fe_3O_4/PAA exhibited maximum ion adsorption. As the amount of polymer-coated magnetite nanoparticles increases, the penetration of ions becomes more difficult, reducing water adsorption. Naturally, this is due to the different chemical compositions of the waters when compared to seawater. It is known that the average salinity of the Caspian Sea water is 12.85%, with carbonates and sulfates being predominant, while chlorides are less prevalent. In the formation waters of the Absheron Peninsula regions, the concentration of $CaCl_2$ is high, with mineralization ranging from 3.1 to 45.5 g/L. Depending on the location, the amounts of Na^+ and Cl^- ions in formation waters are 0.8-15.1 and 0.8-26.4 g/L, respectively. The richer chemical composition of formation water also affects the adsorption capacity of concrete. Compared to inorganic ions, the presence of organic molecules and dispersed oil emulsions in the composition hinders the penetration of ions to some extent. However, in both water samples, the adsorption is characterized by maximum values in the concrete containing 1-1.25% PAA/Fe_3O_4. The concrete filled with PAA/Fe_3O_4 shows 2-4% more adsorption in seawater. However, in both water environments, as the amount of PAA/Fe_3O_4 filler in the concrete samples increases, adsorption begins to decrease. This is due to the magnetite nanoparticles forming stable chemical bonds with the cement components and PAA, altering the surface structure of the concrete. Magnetite nanoparticles chemically interacting with calcium and aluminum silicates in the cement result in the formation of complexes that cannot be hydrated on the surface and in the volume. Additionally, more pores in the concrete being blocked by PAA/Fe_3O_4 complexes limit the penetration of ions in the environment. The adsorption impact of magnetite nanoparticles was also tested in PAA/concrete samples. It was found that adsorption values in PAA-containing concrete in the same waters were 1.3-2.1% higher compared to magnetite nanoparticle concrete. This can be explained by the hydrophilic tendency of PAA macromolecules. Kinetic measurements over 40 days suggest that adsorption stabilizes, and mass change ceases. However, kinetic mass change should be calculated over a longer period. For this purpose, research in this area is currently ongoing, and results will be re-evaluated for at least one year. Nevertheless, concrete samples filled with 2% PAA/Fe3O4 magnetite nanoparticles can be used to construct durable pillars resistant to seawater. Also, it is possible to create long-term barrier rings from those cement pastes by cementing the well bottom zone and the back of the pipeline in the oil industry.

Adding 1% and 2% magnetite nanoparticles by weight to the concrete caused some structural changes. The chemical interaction of magnetite nanoparticles with Ca and Al silicates in the cement led to a reduction and shift in the intensity of the characteristic peaks observed in the XRD patterns of the concrete. These changes indicate that the magnetite nanoparticles chemically interacted with the di- and trisilicates of Ca and Al in the cement. The new peaks also suggest that the magnetite nanoparticles were immobilized in the cement pores without significant size change.

The chemical interaction between magnetite nanoparticles and cement components was also analyzed using FTIR. The chemical interactions formed between di- and tri-Ca silicates in the cement, PAA macromolecules, and magnetite nanoparticles were reflected in the absorption bands of the FTIR spectra. Electron density accumulation in functional groups and oxides led to deformation and vibration changes in the chemical bonds due to chemical interactions. Comparative analysis of the FTIR spectra of free PAA, hydrated cement without polymer, and 1% PAA-added cement was performed. It was determined that the primary chemical shift in the modified PAA was the amine group, which shifted from 1620 cm^{-1} in the polymer to an absorption band at 1632 cm^{-1} in the concrete, indicative of chemical interaction with calcium and aluminum ions and their silicates in the cement. This is because the amine group with a certain electron density enters into coordination with Ca^{2+} and Al^{3+} ions in cement. Additionally, the absorption band corresponding to the carbonyl group in the polymer shifts from 1662 cm^{-1} to 1675 cm^{-1}. All these observations indicate the interaction between PAA and cement particles, which is not observed in the FTIR spectrum of the pure concrete sample.

In the oil and gas sector, the use of cement products for the separation of water and sand in wellbore zones has long been recognized as the most promising technology. It is possible to strengthen the physical and mechanical properties of concrete by adding various transition metals, their composites with polymers, as well as metal nanoparticles to the cement solution. Furthermore, evaluating the environmental sensitivity of metal nanoparticles can lead to interesting findings regarding the behavior of concrete in various mineralized waters. In another study [94], 1.0 and 2.0% (w/w) magnetite nanoparticles of 30–50 nm size were added to cement paste modified with 1% (mass) PVPr, and the adsorption capacities of the hardened stone in formation water and seawater were tested after 28 days. Concrete samples containing 1% PVPr and 2% Fe_3O_4 nanoparticles show the same adsorption capacity. However, concrete with 1% magnetite nanoparticles exhibits 4-6% more mass increase in both seawater and formation water. The increase in the penetration of cation and anion hydrates with the proportional increase in the amount of magnetite nanoparticles is related to another factor. It is possible that magnetite nanoparticles are not protected during localization in the concrete structure. Due to the high surface energy of the specific surface, nanoparticles easily interact with hydrated ions. This relationship is proportional to the concentration of magnetite nanoparticles, leading to faster and higher penetration of hydrated ions in the PVPr/concrete sample with 1% Fe_3O_4. Despite chemical differences between wellwater and seawater compositions, the penetration of ions into magnetite nanoparticle concrete occurs to the same extent. It seems that the difference in adsorption occurs not with the concentration of cations and anions, but with their hydrate form. Polarized water dipoles can form electrostatic interactions with magnetite nanoparticles.

Numerous studies have demonstrated that the incorporation of nanoparticles significantly enhances the mechanical properties and durability of cement-based materials. Nanoparticles contribute to a more compact microstructure, mitigate crack formation, and improve compressive and flexural strengths [95]. In addition, they accelerate the hydration process and promote the formation of well-developed C-S-H phases, resulting in superior mechanical performance. These advancements underscore the potential of nanoparticles as effective modifiers for the design of next-generation high-performance cementitious composites. The incorporation of magnetite (Fe_3O_4) nanoparticles into cement-based materials has been shown to significantly enhance their mechanical properties [96].

These nanoparticles contribute to a denser and more homogeneous microstructure, thereby improving compressive strength and reducing microcrack formation. Additionally, magnetite nanoparticles can accelerate hydration processes and refine pore structure, resulting in improved durability and long-term performance.

Conclusion

Research on cement solutions with added polymers and metal nanoparticles shows that this field is one of the promising and relevant directions. Polymer macromolecules and nanoparticles play significant roles from the initial hydration stage of cement to its complete hardening. They do not hinder the hydration process, but can distribute regularly and irregularly between particles in the structure. In both cases, chemical bonding or electrostatic forces occur between base particles and polymer/nanoparticles. This bond formation results in the formation of superior properties in concrete, improves quality, and enhances durability. Studies confirm that when polymer and metal nanoparticles are added to water rather than directly to cement powder, the pozzolanic effect in concrete becomes more pronounced. Achieving equal immobilization of particles on both the surface and within the concrete matrix becomes possible. At this point, nanoparticles and polymer chains interact with di- and tricalcium silicates and aluminates in cement due to their functional groups, leading to enhanced chemical interaction. This, in turn, results in clearer benefits in the final properties of the concrete. Considering that concrete is the primary structural material, the use of Fe_3O_4 nanoparticles as a filler creates a nano-reinforcement effect, which is progressive in increasing the material's strength properties. Therefore, based on a brief review, the use of metal nanoparticles, especially magnetite and polymer materials, in the dispersed phase in cement products is more appropriate and purposeful.

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