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INVESTIGATION OF MASS GRADIENT OF CONCRETE FILLED WITH POLYACRYLAMIDE/Fe₃O₄ MAGNETITE NANOPARTICLES IN CASPIAN SEA AND FORMATION WATER MEDIUM

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Abstract: In the study, changes in the mass of concrete filled with polyacrylamide/Fe₃O₄ nanoparticles in an amount of 1–2% of the cement mass in sea and formation water were studied. Besides, by performing IR and X-ray characterization of the prepared samples, the chemical state of the polyacrylamide (PAA) and the nanoparticles in the structure was also determined. Changes in mass of concrete samples containing PAA/Fe₃O₄ nanoparticles in highly mineralized seawater were shown to be highly dependent on the amount of nanoparticles compared to PAA. It revealed that at 2% PAA-Fe₃O₄/concrete, the ion penetration was limited and there was a lower weight gain as compared to the control concrete. IR spectroscopic analyses proved that the polymer was in a coordination band with cement and magnetite nanoparticles. X-ray diffraction studies showed a slight increase in the crystallinity of the concrete filled with up to 2% PAA/Fe₃O₄ magnetite nanoparticles.

Keywords: cement, polyacrylamide/Fe₃O₄ nanoparticles, formation water, adsorption

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Introduction

As is known, the concrete is an irreplaceable material used in all areas of modern construction. Historically, cement mixes used volcanic ash, limenit, and seawater, but today engineers also use Portland cement being mixed with aggregates such as gravel and sand [1]. When the concrete comes into contact with certain chemicals such as acids, it reacts with the calcium hydroxide in the cement and forms water-soluble calcium compounds, which are then washed out [2]. Although cement itself is a good curing agent, however, it tends to crack very quickly. The concrete mixed with various aggregates becomes stronger and can maintain its durability for hundreds or even thousands of years. Among these additives, polymers significantly improve the quality of

concrete, making it more durable [3].

The effect of polymer additives on the performance of cemented materials undoubtedly depends on their molecular structures. Studies found that an increase in the molecular weight of polyacrylamide (PAA) leads to a significant decrease in the fluidity of the modified cement paste and the improvement in plastic viscosity [4]. In general, the use of PAA as an overdose has an accelerating effect on the carbonization of cement paste [5]. Another study revealed that calcium ions lead to the cross-linking of anion PAA and the formation of PAA micro-gels [6]. In another study [7], there is an increase in the compressive strength of the concrete made of PAA-added cement, which is explained by the

formation of additional bonds in this composition.

The polymer shows a potential effect on the early deformation and wetting of the cement material. However, there are few studies on hydration kinetics and hydration properties of internal hardening cement material [8,9]. In some studies, active hardening control methodologies based on magnetic fields are applied to reduce leakage of cement materials under active pressure. It showed that the amount

of Fe_3O_4 nanoparticles needed to reduce leakage must be controlled [10].

Considering the above, the kinetics of mass gain in sea and formation water of concrete filled with PAA/ Fe_3O_4 magnetite nanoparticles was studied in the presented study. Also, the IR spectrum and X-ray diffractograms of PAA/ Fe_3O_4 concrete were analyzed and explained the property change in terms of chemical interaction.

Experimental part

Materials

Portland cement of G branded (intended for hardening of well zones API Specification 10A-2011) and high average molecular mass PAA (CAS 9003-05-8, average molecular mass 6000 kDa) and distilled water were used in the preparation of concrete mixtures. Chloride salts of II and III valence of iron were used to obtain magnetite nanoparticles, and 25% NH_4OH solution to transform them into hydroxide form.

Preparation of samples

The mixture of cement with water prepared in a ratio of 0.5 water/cement (w/c). PAA was used up to 1.0% of the dry mass of the cement to be taken. Polymer/magnetite

nanoparticles were initially synthesized for the preparation of concrete samples modified PAA/ Fe_3O_4 . The synthesis was carried out according to the [11] method.

Water absorption of concrete samples was determined by gravimetric method in accordance with AZS 572.3-2011 [12]. The prepared fresh cement pastes were stored in molds with dimensions of $20 \times 20 \times 20$ mm for the complete solidification was expected. Thus, after 28 days, the fully hardened concrete samples were completely dried in 2 days at 40°C and adsorption percentages (A_s) were calculated by keeping them in the Caspian Sea and formation water periodically for 40 days.

$$A_s = \frac{W_n - W_0}{W_0} \times 100$$

Where, W_0 = dry mass of cement stone (g), W_n = is the moisture mass of cement stone after keeping it in water for a certain time (g).

Characterization

The type of chemical bonding between macromolecules and cement particles and between nanoparticles and silicates in simple cement concrete samples with the addition of

PAA and PAA/ Fe_3O_4 was determined using a Fourier transform infrared spectroscopy (FTIR) (Nicolet FT-IR Avatar 360). The crystalline phase in the ordinary concrete, the concrete/PAA and PAA/ Fe_3O_4 concrete samples were examined using an X' Pert-Pro MPD diffractometer (Cu- K_α source, $k=0.15405$ nm).

Results and Discussion

It is known that the regulation of the concrete composition during operation depends on the environmental conditions and the place of application [3]. The most important impact to consider are ambient temperature and water chemistry – salinity. In the present work, concrete samples were prepared by adding

magnetite nanoparticles synthesized in a polyacrylamide medium to Portland cement. After 28 days of complete curing of the resulting hardened stone, changes in the mass of the *Caspian Sea* and formation water were examined and compared to control concrete (Fig. 1). It revealed that the control concrete and

the concrete containing 2% (w/w) PAA/Fe₃O₄ nanoparticles underwent the adsorption process to the same extent within 10 days. The concrete with 1% PAA/Fe₃O₄ nanoparticles shows mass

increase of 4–4.5% and the adsorption mass change in the sample occurs by up to 15% within 40 days.

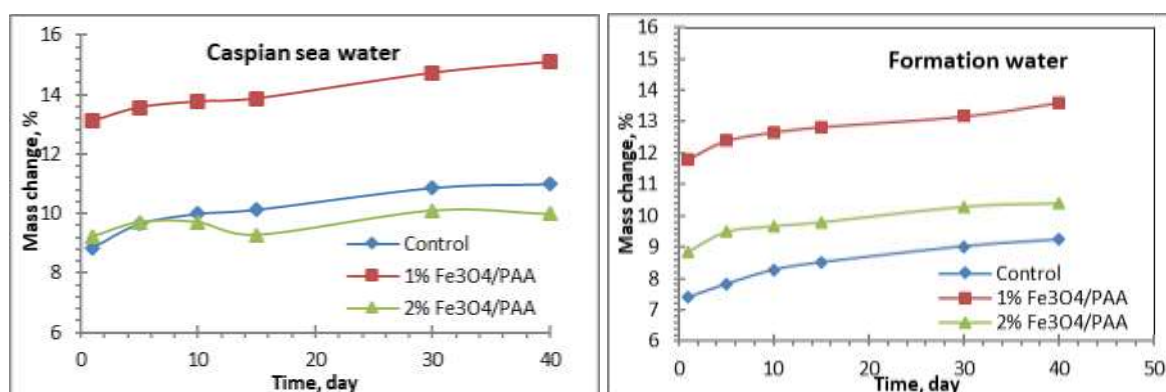


Fig. 1. Adsorption kinetics of PAA/Fe₃O₄ magnetite nanoparticle modified concrete in the *Caspian Sea* and well-bore water medium.

As can be seen, concrete with 2% PAA/Fe₃O₄ nanoparticles has limited ion penetration and even experiences a smaller mass change as compared to the control concrete. In general, in all cases, after 40 days it is clear that the weight gain stabilizes. The high adsorption in the concrete sample with 1% PAA/Fe₃O₄ nanoparticles is believed to be due to magnetite particles. PAA macromolecules only ensure the stability of the size of magnetite nanoparticles over a long period of time. Thus, the distribution of PAA-containing magnetite nanoparticles on the surface in a concentration of 1% (by weight) leads to the formation of pores that allow water molecules to penetrate into the inner layers. As the concentration of magnetite nanoparticles increases, the penetration of salt ions and water molecules becomes more difficult due to the hydrophobicity of the concrete surface. Since adsorption only occurs on the surface, iron oxides prevent hydration from penetrating the concrete.

Observations in produced water have yielded relatively different results as compared to seawater. In the control concrete sample, an increase in the formation of water mass of 9–9.2% was observed over 40 days. In the concrete modified with PAA magnetite nanoparticles, the adsorption of formation water increases as the number of nanoparticles increases. But even in this case, the concrete

filled with 1% Fe₃O₄/PAA shows maximum ion adsorption. As the number of magnetite polymer nanoparticles increases, water adsorption decreases as ion penetration becomes more difficult. As compared to seawater, this is of course due to the different chemical composition of the waters. It is known that the average mineralization of the waters of the Caspian Sea is 12.85%, with carbonates and sulfates accounts for the majority and chlorides accounts for the minority [13]. In the formation of waters of the Absheron Peninsula zones, the density of CaCl₂ is high and the mineralization varies between 3.1 and 45.5 g/L [14]. Depending on the location, the amount of Na⁺ and Cl⁻ ions in the formation water is 0.8–15.1 and 0.8–26.4 g/L, respectively. The richer chemical composition of the formation water also affects the adsorption ability of the concrete. As compared to inorganic ions in the composition, the presence of organic molecules and dispersed oil emulsions makes it difficult for ions to penetrate. However, in both water samples, the adsorption in the concrete with a PAA/Fe₃O₄ content of 1–1.25% is characterized by a maximum value. If one considers the adsorption values depending on the amount of PAA/Fe₃O₄ nanoparticles in the composition, the pattern becomes clear (Fig. 2).

As can be seen from Fig. 2, the concrete filled with PAA/Fe₃O₄ exhibits relatively higher adsorption in seawater of 2–4%. However, as the

content of PAA/Fe₃O₄ filler increases in both water concrete samples, the adsorption begins to decrease. This is due to the fact that magnetite nanoparticles change the structure of the concrete surface after constant chemical contact with the components of cement and PAA. Thus, the entry of magnetite nanoparticles into a

chemical bond with calcium and aluminum silicates in cement leads to the formation of complexes that are not hydrated on the surface and in the bulk. Also, the large blocking of pores in concrete by PAA/Fe₃O₄ complexes limits the penetration of ions into the environment.

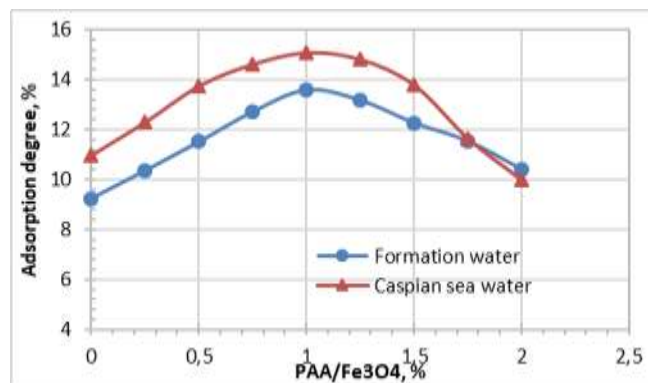


Fig. 2. Adsorption data depending on the amount of PAA/Fe₃O₄ in % of concrete stone formation and Caspian Sea water. For 40-day hardened concrete specimens.

The effect of magnetite nanoparticles on adsorption was also tested on a PAA/concrete sample. It was established that PAA concrete has adsorption rates that are 1.3-2.1% higher in the same water than the concrete with magnetite nanoparticles. This can be explained by the tendency of PAA macromolecules to be hydrophilic. Kinetic measurements carried out over 40 days suggest that adsorption gradually stabilizes and mass does not change. Of course, kinetically, the change in mass should be calculated over a longer time. To this end, our research is ongoing, and the results will be reviewed for at least a year. However, seawater-resistant structural columns can be made from

concrete samples filled with 2% PAA/Fe₃O₄ magnetite nanoparticles. Also, these cement pastes can be used to create long-term barrier rings by cementing the bottom-hole zone of wells and the back of the pipeline in the oil industry.

Changes in the structure as a result of the inclusion of magnetite nanoparticles in the composition of concrete samples were studied using X-ray phase diffractograms. It is known that [13] in the XRD spectrum of plain concrete $2\theta = (25.2^\circ), (29.1^\circ), (32.4^\circ), (34.5^\circ), (41.3^\circ), (47.5^\circ), (50.8^\circ),$ and (51.7°) - specific peaks for di- and tricalcium silicates, as well as calcium-aluminum silicates are observed (Fig.3).

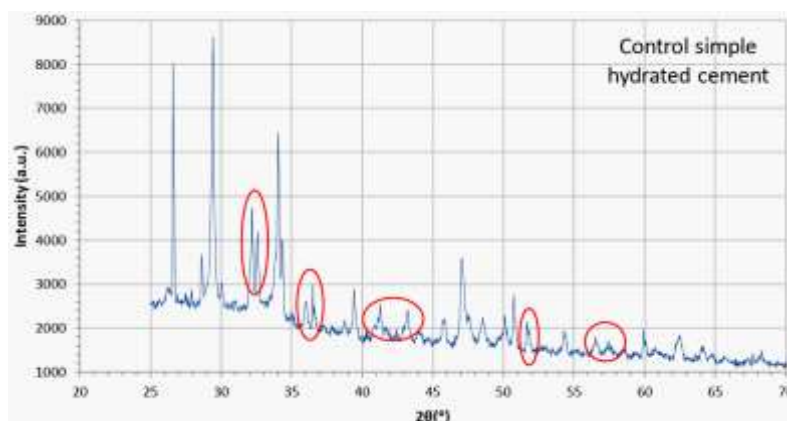


Fig. 3. XRD diffractogram of the control concrete sample after 28 days of aging

On the other hand, the XRD patterns for pure magnetite Fe_3O_4 nanoparticles, $2\theta = 30.17^\circ$, 35.58° , 43.53° , 53.80° , 57.50° , 63° , and 74.35° at (220), (311), (311), (400), (422), (511), (440), and (553) field diffractograms were characteristic, respectively [14]. The inclusion of magnetite nanoparticles in the amount of 1 and 2% of cement in the concrete composition causes some changes in the structure. The interaction of magnetite nanoparticles with Ca and Al silicates in cement causes a decrease in the intensity of peaks characteristic of the concrete in XRD (Fig. 4).

The peaks outlined in red in Fig.3 were

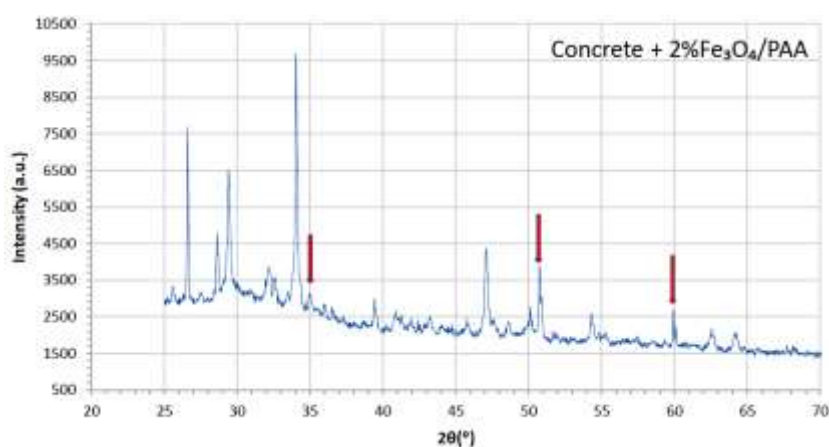


Fig. 4. XRD diffractogram of concrete filled with 2% magnetite nano $\text{Fe}_3\text{O}_4/\text{PAA}$ particles

The chemical interaction between magnetite nanoparticles and cement components was also analyzed by FTIR. Thus, the chemical interaction formed between di- and tri-Ca-silicates in cement and the PAA macromolecule, as well as magnetite nanoparticles, manifests itself in the absorption of absorption bands in the FTIR spectrum of the samples. The electron

density collected in chemical bonds characteristic of functional groups and oxides causes certain deformations and vibrations along the bond due to chemical interaction [15]. Thus, comparative analyzes of the FTIR spectra of free PAA, hydrated concrete without polymer (Fig. 5) and concrete with the addition of 1% PAA (Fig. 6) were carried out.

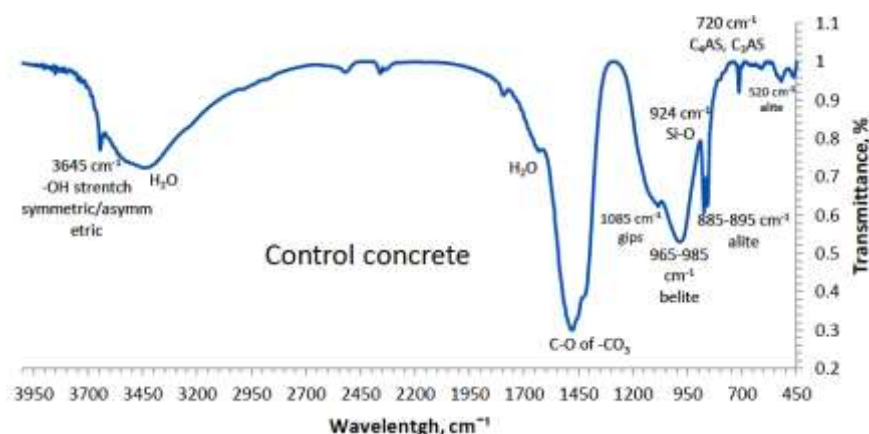


Fig. 5. FTIR spectrum of concrete made with a water/cement ratio of 0.5. After 28 days of curing

For each sample, characteristic absorption bands related to bonds transformed during hydration and modification were monitored. It found that after the modification of PAA, the main chemical shift is the amino group in the polymer and the characteristic absorption bands

of calcium and aluminum ions in cements and their silicates. Thus, the absorption band at 1620 cm^{-1} , related to the N-H bond in the amino group of the polymer, is chemically shifted to the region of 1632 cm^{-1} in the concrete.

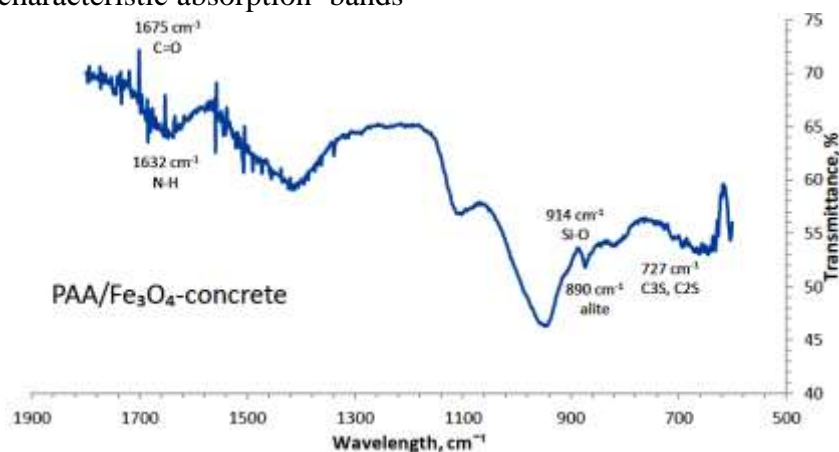


Fig. 6. FTIR spectrum of PAA filled concrete

The above is due to the fact that the amino group with a certain electron density enters into coordination with the Ca^{2+} and Al^{3+} ions in the cement. Violation of the electronic density of bonds in functional groups participating in the main ionic interaction also affects nearby functional groups. Also, the absorption peak around 720 cm^{-1} for C_4Al and C_3Al ferrites shifts to 727 cm^{-1} in PAA-modified concrete. In

addition, the symmetric N-H stretching mode around 3201 cm^{-1} is chemically shifted to 3212 cm^{-1} . Also, the stretching mode of the carbonyl group in the polymer shifts from 1662 cm^{-1} to 1675 cm^{-1} . All this proves the interaction of PAA with cement particles. This type of shift was not detected in the FTIR spectrum of the pure concrete sample.

Acknowledgment

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POLIAKRİLAMİD/Fe₃O₄ MAQNƏTİT NANOHİSSƏCİKLƏRİ İLƏ DOLDURULMUŞ BETONUN XƏZƏR DƏNİZİ VƏ LAY SUYU MÜHİTİNDƏ KÜTLƏ QRADİYENTİNİN TƏDQIQI

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Xülasə: Təqdim olunan məqalədə sementin kütləsinin 1-2% miqdarında poliakrilamid/Fe₃O₄ nanohissəcikləri ilə doldurulmuş betonun dəniz və lay suyunda kütlə dəyişiklikləri öyrənilmişdir. Eləcə də, hazırlanmış nümunələrin İQ və rentgen xarakteristikaları aparılmaqla polimer və nanohissəciklərin strukturda kimyəvi halı müəyyənləşdirilmişdir. Göstərilmişdir ki, PAA ilə müqayisədə PAA/Fe₃O₄ nanohissəcikli beton nümunələrin yüksək mineralli dəniz suyunda kütlə dəyişimləri nanohissəciklərin miqdarından kəskin asılıdır. 2%-li PAA-Fe₃O₄/betonda isə ionların nüfuzu limitlənir və kontrol betonla müqayisədə daha kiçik kütlə artımına məruz qalır. Rentgen quruluş tədqiqatları isə 2%-ə qədər PAA/Fe₃O₄ nanohissəcikləri ilə doldurulmuş betonun kristallılığının cüzi artdığını göstərir.

Açar sözlər: sement, poliakrilamid, maqnetit, nanohissəciklər, adsorbsiya.

**ИССЛЕДОВАНИЕ ГРАДИЕНТА МАССЫ БЕТОНА, ЗАПОЛНЕННОГО
НАНОЧАСТИЦАМИ ПОЛИАКРИЛАМИДА/ Fe_3O_4 МАГНЕТИТА, В КАСПИЙСКОМ
МОРЕ И ПЛАСТОВОЙ ВОДНОЙ СРЕДЕ**

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Аннотация: В представленной статье исследованы изменения массы бетона, наполненного наночастицами полиакриламида/ Fe_3O_4 в количестве 1-2% от массы цемента, затворенного в морской и пластовой воде. Также путём проведения ИК- и рентгеновских характеристик приготовленных образцов определяли химическое состояние полимера и наночастиц в структуре. Показано, что изменение массы образцов бетона с наночастицами ПАА/ Fe_3O_4 в высокоминерализованной морской воде сильно зависит от количества наночастиц по сравнению с ПАА. В случае 2%-го ПАА/ Fe_3O_4 проникновение ионов в бетон ограничено и происходит меньшее увеличение массы по сравнению с контрольным бетоном. Рентгеноструктурные исследования показывают незначительное увеличение кристалличности бетона, наполненного до 2% наночастицами ПАА/ Fe_3O_4 .

Ключевые слова: цемент, полиакриламид, магнетит, наночастицы, адсорбция.