

INFLUENCE OF STARCH ADMIXTURES AND SILVER COLLOIDS STABILISED WITH STARCH HYDROLYSATES ON THE COURSE OF ELECTROCHEMICAL POTENTIAL DIFFERENCE OF REINFORCING STEEL IN HIGH-CHLORIDE ENVIRONMENT

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Abstract

The purpose of the conducted study was to verify whether the use of concrete admixtures with modified starches and starches modified with stabilised silver colloids affects the course of electrochemical potential difference, and hence corrosion, of reinforcing steel in a chloride environment. In the tests, cross-linked starches and products of acid hydrolysis of starch (dextrins) were used as admixtures. The 1-molar aqueous solution of sodium chloride was used as an aggressive environment. The tests consisted of measuring the potential difference generated in the reinforcement corrosion cell on the surface for a period of 60 days and then assessing the risk of corrosion. The effect of the addition of starch derivatives on the properties of cement paste was investigated through a one-way ANOVA analysis of variance followed by *post hoc* tests. The test results showed that the use of concrete admixtures with cross-linked starches positively affects the passivation of the steel. The likelihood of reinforcing steel corrosion when using distarch phosphate, acetylated distarch phosphate and acetylated distarch adipate admixtures is less than 5%. The results obtained showed an improved effect on the passivation of reinforcing steel in cement composites. Additionally, concrete samples may have microbicidal properties.

Keywords: concrete, cement paste, dextrins, electrochemical corrosion, nanosilver

1. INTRODUCTION

The necessity of designing and constructing highly complicated concrete structures exploited under challenging conditions forces scientists and designers to search for new-generation concretes that demonstrate greater durability, strength, environmental compatibility, and other sustainable properties that have so far been unattainable.

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According to PN-EN 206+A2:2021 [1], the expected design life of concrete structures should not be shorter than 50 years, while the value for bridges should be 100 years. Global sustainability concerns result in a tendency to go beyond this time. Bridge design in Australia can serve as an example, with a design life of 100 years planned to be extended to 125 years [2].

Factors that affect reinforced concrete damage, both in the concrete cover and steel reinforcement in reinforced concrete elements, can be distinguished as those associated with the type of concrete and reinforcement and those conditioned by the surrounding environment. Damage caused by carbonisation and erosion from chloride ions of the passive layer of steel bars is one of the most important factors causing the corrosion of steel bars. The carbonation phenomenon causes calcium hydroxide in concrete to react with carbon dioxide, destroying the alkaline passive film. The corrosion of chloride ions means that free chloride ions can corrode the passive layer and improve conductivity, thus accelerating reinforcement corrosion [3].

The search for better protection of reinforcing steel to mitigate corrosion in reinforced concrete elements and study the mechanism of corrosion has been the subject of research by numerous scientists [4–9]. An example of this is the use of galvanised reinforcement bars by Loto [10] and Jasniok *et al.* [11], Cr-modified reinforcing steel by Shi *et al.* [12], or waterproofing membranes and epoxy coatings by Broomfield [13]. Loto and Okusanya [14], to eliminate the corrosion effect of reinforcement caused by the carbonisation of concrete, suggest the use of stainless steel in structures. Stainless steel exhibits good passivation properties in an alkaline environment; however, on a very frequent basis, in contact with aggressive anions (i.e. chlorides), the created protective film can be damaged. Numerous studies have shown that stainless steel undergoes pitting and crevice corrosion [15]. In most cases, pitting damage caused by the use of stainless steel is the result of chloride ions. The scale of damage depends on the concentration of chlorides in a medium, e.g., in a seawater environment. Recently, attention has been drawn to the development of natural and environmentally friendly corrosion inhibitors, such as casein [16], white aluminium dross [10], red mud, fly ash [17–20] ground granulated blast furnace slag [21], cactus mucilage and brown seaweed extracts [22], or leaf extract of *disporopsis pernyi* [23]. Salami *et al.* in their article [24] provided a critical review of the state of the art on corrosion studies performed on AAB (alkali-activated binders) with different precursor materials subjected to a chloride environment.

Chlorides from seawater are extremely hazardous since they accelerate the processes of depassivation and corrosion of reinforcing steel. The effect of seawater on concrete is very complex due to the quantity and concentration of chemical compounds dissolved in it and the varied nature of their effect on concrete. The average pH value of seawater is usually 8.1 ± 0.1 [25,26].

Designing chloride-resistant concrete, which increases the service life of reinforcing steel, is particularly important in the case of marine structures such as breakwaters, coastal structures, docks, retaining walls, road structures, tunnels, and bridges where road salt is used. Moreover, public buildings exposed to chlorine compounds, such as hospitals, swimming pools, etc.

The European Standard PN-EN 1504-9: 2010 [27], concerning products and systems for the protection and repair of concrete structures, presents methods for the protection and repair of reinforced concrete structures. These include the following:

- increase in concrete cover thickness of reinforcement;
- replacement of contaminated or carbonated concrete;
- realkalisation of carbonated concrete by diffusion;
- electrochemical removal of chlorides;
- increase in electrical resistance of the concrete thickness;
- control of cathodic areas;
- cathodic protection, control of anodic areas.

Due to the electrochemical nature of the corrosion processes that occur in reinforced concrete structures, several methods are used for diagnostic tests. They determine the probability of corrosion in reinforcement (that is, measurement of stationary potential and resistivity of concrete cover) or the rate of corrosion progress in reinforcement (that is, polarisation method) [3,28–30].

The research conducted has shown that the doping of cement slurries, mortars, and concretes with starch hydrolysates influences their physicochemical parameters. The admixture of dextrans affects the rheology of the cement mixture, improving its workability and significantly lowering the flow limit. In addition, a 20% increase in the strength of cement mortars and concretes was observed without lowering the water-cement ratio [31]. Research also showed a positive effect of dextrans on the frost resistance of cement concrete, thus improving its durability [32]. In [31] the authors showed that cement composites doped with colloidal silver stabilised with dextrans were characterized by high antimicrobial activity. A nanosilver admixture in concrete can protect structures against the activity of microorganisms, thus increasing the durability and aesthetics of constructed objects. To increase the durability of a structure, additional concrete admixtures can be used to protect steel elements against the intensive action of chlorides. For the purpose of the study it was decided to carry out some tests using 0.5% starch admixtures in the form of starch hydrolysates and cross-linked starches.

Because the synthesis of silver nanoparticles with selected starch derivatives is quite simple, it was decided to create admixtures that, in addition to influencing steel passivation, would give microbicidal properties of the produced biocomposites.

2. MATERIALS AND METHODS

2.1 Materials

The tests were carried out using starch admixtures in the form of dextrans (0.5% d/c) and crosslinked starches (1% d/c). They also covered the effect of admixture with nanosilver stabilised with starch on steel passivation. The substances used in the study are presented below:

- White dextrin (hereinafter called d2);
- Yellow dextrin (d3);
- White dextrin with the addition of nanosilver (d2 + 60ppm AgNPs);
- Yellow dextrin with the addition of nanosilver (d3 + 60ppm AgNPs);
- Distarch phosphate, low degree of cross-linking (E1412L);
- Distarch phosphate (low degree of cross-linking) with the addition of nanosilver at a concentration of 60 ppm (E1412L + 60 ppm AgNPs);
- Distarch phosphate (low degree of cross-linking) with the addition of nanosilver at a concentration of 300 ppm (E1412L + 300 ppm AgNPs);
- Distarch phosphate, high degree of cross-linking (E1412H);
- Acetylated distarch phosphate (E 1414);
- Acetylated distarch phosphate with the addition of nanosilver at the concentration of 60 ppm (E1414 + 60 ppm AgNPs);
- Acetylated distarch phosphate with the addition of nanosilver at the concentration of 300 ppm (E1414 + 300 ppm AgNPs);
- Acetylated distarch adipate (E1422).

The starch derivatives used in the study were produced by WPPZ S.A. (Poland).

The precursor for the production of nanostructured silver was diaminasilver (I) cation $[\text{Ag}(\text{NH}_3)_2]^+$, with a silver content of 4 g/dm³. The concentration of starch derivative in the reaction

mixture was 20 g/dm^3 . The synthesis was carried out at a temperature of 45°C to prevent complete gelatinization of the starch. The reaction mixture was heated with continuous stirring using a magnetic stirrer for a period of 60 minutes.

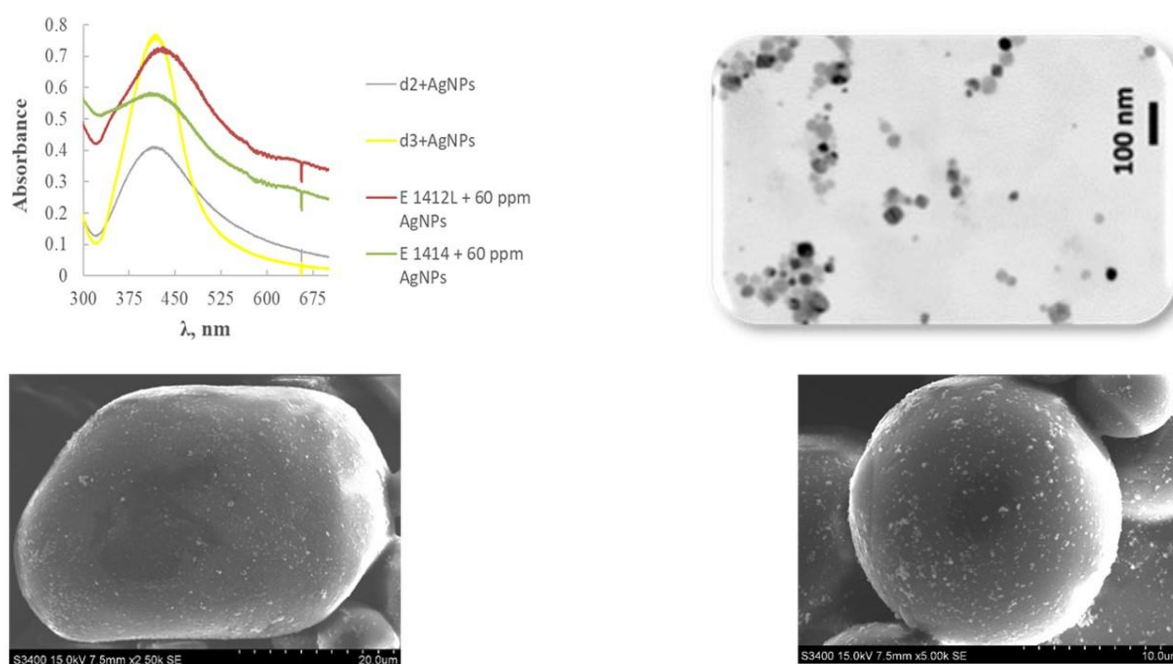


Fig. 1. Physicochemical properties of AgNPs

The heating was then stopped, and the synthesis reaction was carried out with continuous stirring for another 7 days. The selected physicochemical properties of the silver nanostructures used in this research are presented in Fig. 1. The optical absorption spectra were determined with the OceanOptics UV-Vis USB4000 spectrophotometer. All studied solutions displayed a characteristic absorption band at ca. 420 nm, attributed to the presence of silver plasmonic nanoparticles (Fig. 1a). TEM and SEM images were taken using the Jeol1200EX2 microscope operating at 80 kV and the S-3400N microscope (Hitachi), respectively. Fig. 1b shows that the particles produced from the silver colloids stabilised with dextrin are less than 100 nm. In turn, Figs. 1c and 1d show the surface of cross-linked starch grains covered with agglomerates of silver nanostructures.

2.2 Methods

To measure the potential difference in the corrosion cell, 25 mm long cement paste cubes were made, with smooth steel bars (6 mm in diameter, 50 mm long) placed centrally inside. The cover of the underside of the sample was 1 cm thick. To maintain the w/c ratio, the cube mould was made of silicone. Steel bars were cleaned before use. The cement paste samples were made as follows: starch was dissolved in water and then cement was added. The mixture was stirred with a mechanical agitator for 5 min. Each time, the water-cement ratio was $w/c = 0.5$. The amount of starch admixture was 0.5% d/c when using dextrans and 1% d/c for crosslinked starches. The concentration of nanosilver in the sample was 60 ppm or 300 ppm. Steel bars were placed halfway through the cube to ensure that the cement paste cover was of the same thickness on each side. They were also protected against possible

displacement by fixing them on a PET disc. The disc and mould were removed after 24 hours and the prepared sample was left for 14 days in tap water. After this time, the samples were partially immersed in a sodium chloride solution (1 mol/dm^3).

Measurements began 5 days after inserting the sample into the saline solution. They consisted of measuring the potential difference generated in the corrosion cell on the surface of reinforcement. Measurements were taken with the use of a laboratory voltmeter with wires attached to the zinc anode (used as a reference electrode) and a steel rod. For each of the additives studied, a set of three measurements was taken with one minute apart. The measurements were taken with the use of an automatic measurement device to eliminate the effect of external factors on the results. The results presented in the following section are the arithmetic mean of the measurements taken. The research diagram is shown in Fig. 2.

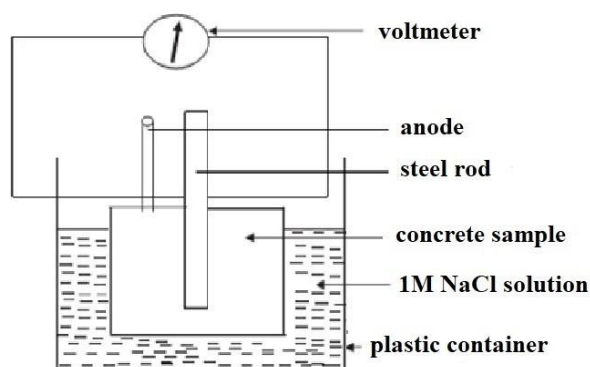


Fig. 2. Research diagram of the system applied to measure the potential difference in the corrosion cell

3. RESULTS AND DISCUSSION

To determine the effect of starch and nanosilver admixtures on reinforced concrete elements, it was decided to carry out electrochemical potential difference tests of reinforced concrete.

Fig. 3 shows the potential differences obtained during a 60-day observation period of reinforced concrete samples with the addition of dextrans (d2 and d3), starch phosphate (E1412L and E1412H), acetylated distarch phosphate (E1414) and acetylated distarch adipate (E1422). The results obtained were compared with the reference values (which did not include starch admixtures).

The change in potential differences in the reference sample proceeded as follows. During the first 14 days of observation, the protective film was gradually damaged, leading to a decrease in the potential difference from -0.49 V to -0.66 V . Subsequently, for the next 2 days, the protective film was recovered (passivation process), causing an increase in the potential difference to -0.43 V . During the following seven days, steel depassivation occurred, which led to a decrease in the potential difference to -0.595 V .

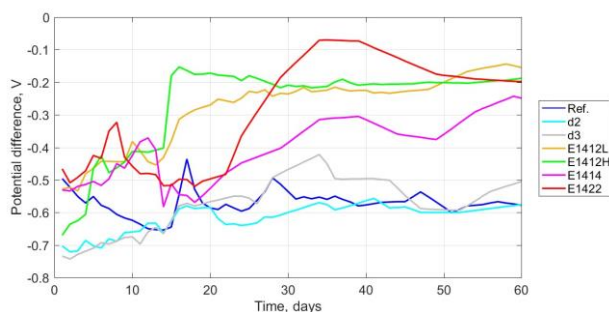


Fig. 3. The potential difference from the exposure time function for reinforced concrete samples with modified starch admixtures immersed in a 1M NaCl solution

The following 4 days allowed a significant recovery of the protective film and an increase in the potential difference to -0.49 V. Over the following days, alternating periods of steel passivation and depassivation were observed. They were characterised by a lower amplitude of fluctuations and finally led to a constant value of the potential difference of approx. -0.58 V. Different behaviours were observed in samples containing starch admixtures. The changing value of the electrode potential was analysed in detail on the example of a sample with acetylated distarch phosphate admixture (E1414).

The first 12 days were characterised by the occurrence of steel passivation. During that period, an increase in the potential difference from -0.535 V to -0.38 V was observed. During the next six days (from the 12th to the 18th day of observation), reinforcement steel depassivation was noticed, that is, damage to the protective film. The following 21 days (from the 18th to the 39th day of observation) were characterised by the occurrence of steel repassivation. Over that time, the value of the potential difference increased to -0.305 V. During the subsequent days of the experiment, further fluctuations in the potential difference were recorded. In the last days of observation, it was possible to notice a certain state of equilibrium. The changes in the potential difference were no longer significant (slight changes in voltage are attributed to electrochemical noise), and the value of the potential difference was close to -0.26 V.

The research presented by Ikotun and Afolabi [33] explains these changes with a process in which reactive Cl^- ions react with starch and its derivatives. According to the authors of the cited work, in the environment they have analysed, there are reactions in which the hydroxyl groups of amylose (OH^-) are replaced by Cl^- ions. The hydroxyl groups released in this way react with sodium ions (Na^+), leading to the formation of sodium hydroxide molecules. The alkalinity of these molecules increases the pH value of the concrete, which facilitates the iron passivation process.

Furthermore, the decrease in concrete pH was probably caused by the penetration of Cl^- ions, which could no longer react with starch derivatives. This led to the reaction of chlorine ions with the iron oxides Fe_2O_3 and Fe_3O_4 , the components of the thin passivation layer, as a result of which iron chlorides were formed, which – after the reaction with water – caused the formation of iron hydroxide and hydrochloric acid [34]. The occurrence of these compounds led, as a consequence, to a further decrease in pH and thus to the deepening of the steel depassivation process. The authors [33] also state that the re-passivation of steel involves an increase in the pH of the concrete. The increase in pH may be due to the increased reactivity of starch and its derivatives under the influence of a lower concrete pH. This increased reactivity again disturbed the constant equilibrium and directed it towards a reaction in which the hydroxide groups of amylose were replaced by chlorine ions (Cl^-), which led to a higher concrete pH (as described in the first stage of passivation).

The above theory would be plausible if the substitution reaction of starch -OH groups with Cl^- anions derived from the dissociation of the electrolyte (NaCl) had its chemical justification.

Unfortunately, this reaction seems unlikely from a chemical point of view. If this reaction occurs at all, then it is marginal and not relevant to the mechanism of steel corrosion prevention described by scientists.

Periodic increases and decreases in the value of the potential difference (Fig. 3) in the graphs were probably associated with the destruction of successive layers of the starch film. The most probable explanation is that the chloride ions present in the system were gradually consumed, reacting with the cement components and causing partial concrete corrosion, and as a result, their concentration in the solution decreased to a level that was not hazardous to the steel oxide layer (balance in the value of the potential difference in the final stage of the study).

The passive coating of reinforcing steel consists mainly of iron oxides Fe_2O_3 and oxyhydroxides FeOOH . Chloride ions, with a small radius, can be adsorbed or easily penetrate the passive layer, even the oxide layer thus damaging its integrity and subsequently accelerating electrochemical reactions. In addition, abundant chloride concentrations, favourable to lower resistivity, also indirectly facilitate electrochemical reactions [21].

The high deposition leads to the formation of $\beta\text{-FeOOH}$, but the low chloride facilitates the accumulation of lepidocrocite ($\gamma\text{-FeOOH}$). $\alpha\text{-FeOOH}$ (goethite) and $\beta\text{-Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$ might be also formed when high chloride concentrations are provided [35]. Another product of the interaction of chlorides with iron may be the formation of "chloride green rust" - compound varied continuously from $\text{Fe}^{\text{II}} 3\text{Fe}^{\text{III}}(\text{OH})_8\text{Cl}\cdot n\text{H}_2\text{O}$, with n probably equal to 2, to approximately $\text{Fe}^{\text{II}} 2.2\text{Fe}^{\text{III}}(\text{OH})_{6.4}\text{Cl}\cdot n\text{H}_2\text{O}$ [36] or $\text{Fe}^{\text{II}} 3\text{Fe}^{\text{III}}(\text{OH})_8\text{Cl}\cdot 2\text{H}_2\text{O}$, $\beta\text{-FeOOH}(\beta\text{-FeO}_{1-x}(\text{OH})_{1+x}\text{Cl}_x)$ [37].

Because of the complex and multifaceted process of chloride interaction on the passive layer of steel, which is a compilation of chemical interactions (increase in solubility, formation of complex compounds), electrochemical interactions (redox reactions, and processes occurring during pitting corrosion), and physical adsorption processes, it seems impossible to write simple chemical reactions.

Moreover, in concrete composite samples, high chloride concentrations are mainly bound to mortar gels as low-solubility calcium-containing compounds (e.g., Friedel salts, calcium chloride), which represent a reservoir of aggressive chloride ions.

The proposed theory also explains why cross-linked starches showed anticorrosive properties, while dextrans did not demonstrate such characteristics. Although their formulas are very similar (a similar number of -OH groups in the weighed amount, they differ only in the presence of a relatively small amount of acetyl and phosphate groups), the pastes of cross-linked starch derivatives are characterised by high density and good texturising properties and, additionally, acetylation causes partial hydrophobization of the chain; therefore, they create permanent films. Dextrans do not create permanent films because their sugar chains are too short.

At this stage, it is worth noting that for the tested admixtures, different processes were observed, as well as different numbers of alternate steel passivation/depasivation were observed. Furthermore, it can be concluded that there was no first passivation period for the reference sample, and the observed sequence of changes in the potential difference began with the depasivation period.

The test results confirm that the addition of dextrans to concrete does not have a negative impact on the steel passivation. On the last day of the 60-day observation, the samples with dextrans did not show a lower value of the potential difference. Furthermore, a detailed analysis of the entire 60-day observation period allows us to conclude that the obtained results of the potential difference were higher than the reference values for most of the starch samples tested. Only dextrans d2 and d3 are characterised by longer periods of lower values of potential difference values compared to reference values. Because of their rheological properties, starch hydrolysates (dextrans) cannot form liquid films at cement grain

boundaries or in pores, unlike cross-linked derivatives. For this reason, they do not improve the passivation protection properties of the reinforcing steel.

Table 1. The potential criterion of reinforcement corrosion hazard in concrete

Criteria for assessing the potential of stationary reinforcement	Probability of reinforcement corrosion [%]
$E_{st} \leq -0.35V$	95
$-0.35V < E_{st} \leq -0.20V$	50
$-0.20V < E_{st}$	5

Measurement results can be evaluated according to the criteria recommended by ASTM C 867-91 [38] and the guidelines provided by Wawrusiewicz [39]. The use of cross-linked starches in the samples resulted in a significant improvement in steel passivation. According to Table 1, the risk of reinforcement corrosion for distarch phosphate (E1412L), distarch phosphate (E1412H) and acetylated distarch adipate (E1422) admixtures is less than 5% (the value of the potential difference is greater than $-0.20V$). When using acetylated distarch phosphate admixture (E1414), the risk of corrosion is 50%. However, for dextrans (d2 and d3) and the reference sample, the corrosion probability is 95%.

Due to the use of nanosilver in the study, we decided to perform measurements using silver colloids to examine whether AgNPs affect the corrosivity of reinforced concrete. Fig. 4 shows the test results for dextrans d2 and d3 both with and without the use of nanosilver, as well as the results for the reference sample.

Fig. 4a presents the data results for the white dextrin d2 as well as for d2+AgNPs. During the first 21 days of observation, the protective film was progressively recovered (passivation process), which led to an increase in the potential difference to 0.58 V. Subsequently, for the next 4 days, the protective film damage (depassivation process) caused a decrease in the potential difference to -0.64 V. During the following 11 days, steel passivation occurred, which led to an increase in the potential difference to -0.57 V. Over the following days, small fluctuations were observed, leading to a -0.57 V potential difference at the end of the experiment. A quite similar course was observed for d2 + AgNPs.

Fig. 4b shows the data results for yellow dextrin d3, d3+AgNPs, and the reference values. The values for d3 on the first 34 days almost constantly recovered the protective film and an increase in the potential difference to -0.42 V was observed. During the following 18 days, steel depassivation occurred, which led to a decrease in the potential difference to -0.59 V. Over the following days, until the end of the experiment, steel passivation occurred, which led to an increase in the potential difference to -0.50 V. In this case, no fluctuation phase was observed (it is recommended that the observation period for this substance be extended). In the case of d3 + AgNPs, during the first 19 days of observation, the protective film was gradually recovered (passivation process), which led to an increase in the potential difference to -0.58 V. This stage was followed by the oscillation phase, which was observed until the end of the experiment.

Fig. 4c shows the results for distarch phosphate E1412L, E1412L + 60ppm AgNPs, E1412L + 300ppm AgNPs, and a reference curve. For all the curves except the reference one, for the first 28 days, a disturbing passivation period resulted in an increase in potential difference to ca. -0.25 V, followed by a fluctuation phase (observed until the end of the final value of the experiment with -0.14 V).

Fig. 4d shows the results for the acetylated distarch phosphate E1414, E1414 + 60ppm AgNPs, and E1414 + 300ppm AgNPs. During the first 12 days of observation, the protective film was progressively recovered (passivation process), which led to an increase in the potential difference to -0.37 V. Subsequently, for the next 6 days, the protective film damage (depassivation process) caused a decrease in the potential difference to -0.57 V. During the following 16 days, steel passivation

occurred, which led to an increase in the potential difference to -0.31 V. For the next 10 days, a decrease in the potential difference was observed, reaching a value of -0.38 V, indicating the depassivation phase. Within the following days, a repassivation process was observed, leading to a -0.25 V potential difference at the end of the experiment. In the case of nanosilver-enriched samples, for the first 15 days, a significant increase in potential difference was observed (up to -0.40 V and -0.30 V for additions with 60 and 300 ppm AgNPs, respectively). This stage was followed by a gentle passivation stage that led to -0.20 V at the end of the experiment.

Furthermore, to emphasise the effect of the analysis on steel passivation, Fig. 5 shows the values of the differential potential of electrodes, that is, the difference in the potential for the reference value was subtracted from the potential of a given substance. This allows a transparent assessment of the effect of individual substances on the passivation properties of steel since positive values mean improvement in properties, and negative values mean their deterioration. The reference value on the graph takes 0 V.

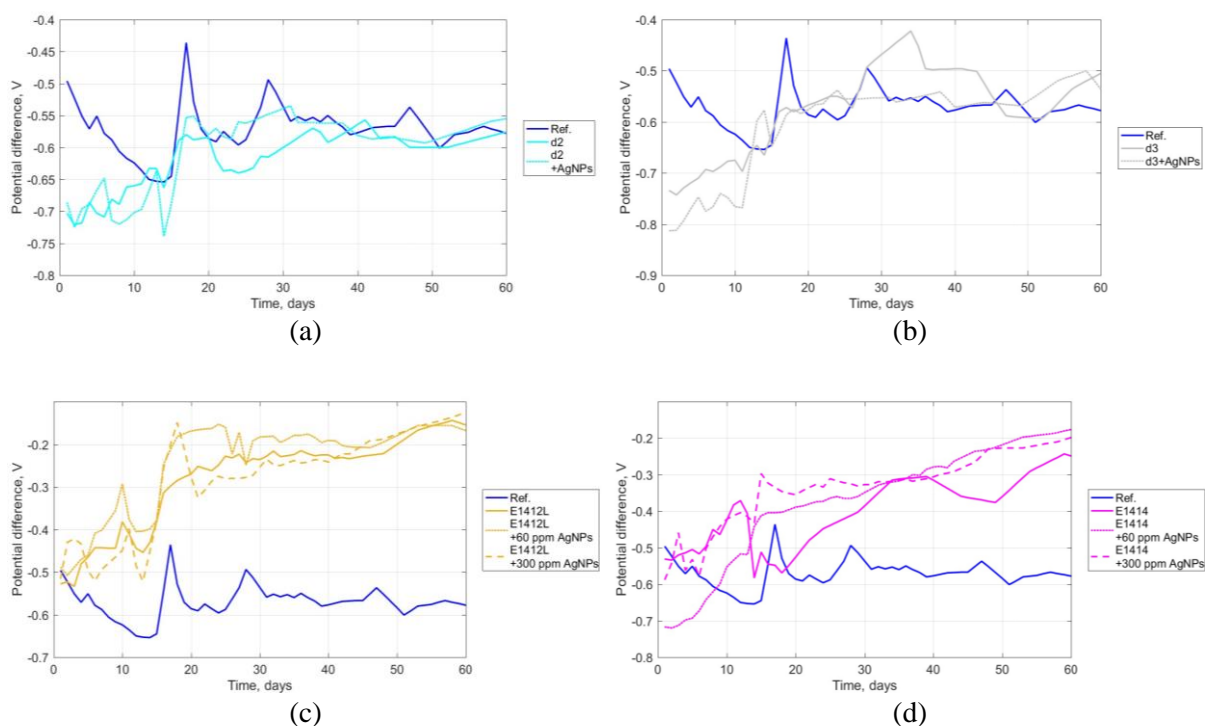


Fig. 4. The potential difference from the exposure time function for reinforcing steel samples with starch derivatives, starch derivatives with nanosilver and without admixtures immersed in a 1M NaCl solution

Based on Fig. 5a, it can be concluded that cross-linked starches allow for the improvement in steel passivation in almost the entire analysed time interval. Only deterioration was observed for distarch phosphate and acetylated distarch phosphate between 16 and 19 days of testing.

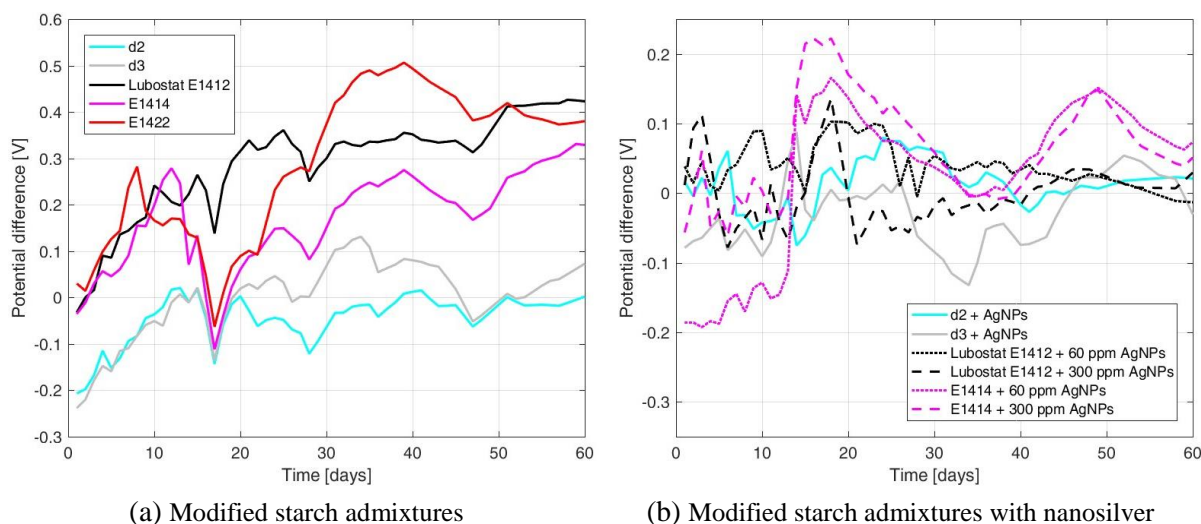


Fig. 5. The potential difference from the exposure time function for reinforced concrete samples, immersed in a 1M NaCl solution

Worse results were observed for those dextrans tested that had significantly negative values on the graphs, which meant worse passive properties than those exhibited by the reference sample. However, note that on the last day of the study, the results obtained for the dextrans were not worse than the results for the reference sample.

A similar differential analysis (Fig. 5b) was also performed for admixtures with nanosilver (the potential difference for a given substance without nanosilver was subtracted from the potential difference for the given substance with nanosilver). This helps to evaluate the effect of nanosilver on the obtained results, where, as in the previous case, positive values mean an improvement in the passivation properties of steel, and negative values indicate their deterioration. On the basis of the above graph (Fig. 5b), it can be concluded that the use of nanosilver affects the passivation of steel insignificantly.

4. STATISTICAL ANALYSIS

To verify whether the results obtained differ significantly, two sets of ANOVA tests followed by a *post hoc* test have been performed [40,41]. Due to the nature of the results observed, statistical analysis was performed after an initial phase of each process, which was decided to be 30 days (it was assumed that after 30 days the results tend to oscillate around an established value and no further depassivation and passivation phases occur).

4.1 Methods

For the first set of analyses, the dextrin type was assumed to be a factor that affects the results. Thus, the following null hypothesis has been made:

H0: The addition of dextrin to concrete has an insignificant impact on the electrochemical parameters of concrete.

H1: The addition of dextrin to concrete has a significant impact on the electrochemical parameters of concrete.

To verify this hypothesis, a single-factor ANOVA was performed. The main test has been preceded by the Shapiro–Wilk test (verifying data normality) and the Levene test (verifying variance homogeneity). The ANOVA results are presented in the Table 2.

Since the obtained p-value is lower than the assumed confidence interval ($\alpha = 0.05$), the null hypothesis is rejected. Therefore, it can be stated that the readings of the substance values are significantly different from each other. If the null hypothesis is rejected, then it is necessary to examine which of the compared communities contributed to this. To do this, the differences between values in each group were tested using multiple comparison (*post hoc*) tests – the Bonferroni correction test. The results obtained are presented in the Table 3.

As shown, only in one case can be assumed that the results do not differ significantly (E1412L vs. E1412H), while in the case of other pairs, the differences are significant. Therefore, it can be stated that the addition of dextrans or modified starches has a significant impact on the physicochemical properties of cement pastes.

4.2 AgNPs Particles

The goal of the second set of analyses is to determine whether the addition of silver nanoparticles to concrete affects the concrete parameters. Thus, the following null hypothesis followed by an alternative hypothesis has been formulated:

Table 2. Single-factor ANOVA results for all starch derivatives

ANOVA: Single factor - Summary						
Groups	Count	Sum	Average	Variance		
Reference	30	-17.0395	-0.56798	0.000177		
Dextrin d2	30	-17.5598	-0.58533	0.000133		
Dextrin d3	30	-15.6736	-0.52245	0.002622		
E1412L	30	-6.08059	-0.20269	0.001034		
E1412H	30	-6.08815	-0.20294	5.03E-05		
E1414	30	-9.62939	0.32098	0.001549		
E1422	30	-4.16374	-0.13879	0.002355		
ANOVA						
Source of variation	SS	df	MS	F	p-value	F-crit
Between groups	6.606822	6	1.101137	973.1085	1.3E-146	2.143453
Within groups	0.229708	203	0.001132			
Total	6	209				

Table 3. Results of post hoc tests for all starch derivatives

<i>Post hoc test (Bonferroni correction) - p-value</i>							
	Reference	Dextrin d2	Dextrin d3	E1412L	E1412H	E1414	E1422
Reference	—	1.32E-06	1.57E-05	7.73E-53	1.07E-73	5.81E-39	1.01E-47
Dextrin d2		—	1.59E-08	1.86E-54	1.28E-77	6.60E-41	6.50E-49
Dextrin d3			—	3.47E-36	6.75E-40	2.63E-24	7.60E-37
E1412L				—	9.67E-01	1.83E-18	1.31E-07
E1412H					—	3.78E-23	1.56E-09
E1414						—	6.74E-23
E1422							—
<i>Post hoc test (Bonferroni correction) - Significance</i>							
	Reference	Dextrin d2	Dextrin d3	E1412L	E1412H	E1414	E1422
Reference	—	yes	yes	yes	yes	yes	yes
Dextrin d2		—	yes	yes	yes	yes	yes
Dextrin d3			—	yes	yes	yes	yes
E1412L				—	no	yes	yes
E1412H					—	yes	yes
E1414						—	yes
E1422							—

H0: The addition of silver nanoparticles to concrete has an insignificant impact on the electrochemical parameters of concrete;

H1: The addition of silver nanoparticles to concrete has a significant impact on the electrochemical parameters of concrete.

The hypothesis will be verified based on the exemplary E1412L dextrin. Similarly to Section 4.1, the main test has been preceded by the Shapiro–Wilk test and the Levene test. The ANOVA results are presented in the Table 4.

Table 4. Results of single-factor ANOVA for AgNPs additions

<i>ANOVA: Single factor - Summary</i>						
Groups	Count	Sum	Average	Variance		
E1412L	30	-6.08059	-0.20269	0.001034		
E1412L + 60 ppm AgNPs	30	-5.43951	-0.18132	0.000322		
E1412L + 300 ppm AgNPs	30	-5.91480	-0.19716	0.001721		
<i>ANOVA</i>						
Source of Variation	SS	df	MS	F	p-value	F-crit
Between Groups	0.007382	2	0.003691	3.59822	0.03152	3.101296
Within Groups	0.089242	87	0.001026			
Total	0.096624	89				

Table 5. Results of *post hoc* tests for AgNPs

additions <i>post hoc</i> test (Bonferroni correction) - p-value			
	E1412L	E1412L + 60 ppm AgNPs	E1412L + 300 ppm AgNPs
E1412L	—	2.38E-03	5.66E-01
E1412L + 60 ppm AgNPs		—	5.98E-02
E1412L + 300 ppm AgNPs			—
<i>Post hoc</i> test (Bonferroni correction) - Significance			
	E1412L	E1412L + 60 ppm AgNPs	E1412L + 300 ppm AgNPs
E1412L	—	yes	no
E1412L + 60 ppm AgNPs		—	no
E1412L + 300 ppm AgNPs			—

In this case, the p-value obtained is also lower than the assumed confidence interval ($\alpha = 0.05$); therefore, the null hypothesis is rejected. Therefore, it can be stated that the readings of the values are significantly different from each other. Since the null hypothesis was rejected, the differences between the values in each group were tested using multiple comparison (*post hoc*) tests, the Bonferroni correction test. The results obtained are presented in the Table 5.

As presented in the Table 5 the only significant difference occurs between the results obtained for E1412L vs. E1412L + 60 ppm AgNPs. The remaining two comparisons indicate that the difference is not significant. Thus, it can be expected that the addition of silver nanoparticles to concrete has a negligible or small impact on the results obtained.

5. CONCLUSIONS

- The use of admixtures with starch derivatives significantly affects the course of the electrochemical potential difference, and hence the corrosion, in cement composites. Based on statistical analysis, it was found that twenty (out of twenty-one) *post hoc* tests showed significant differences between the results.
- The use of cross-linked starches has a positive effect on the passivation of the reinforcing steel and reduces the likelihood of reinforcing steel corrosion in cement composites by up to 5%. This is caused by the increase in the potential difference above the threshold of -0.20 V.
- The use of dextrans does not improve the passivation of the reinforcing steel. Although from a statistical point of view, the results obtained differ significantly, the change in the potential difference is not sufficient to reduce the likelihood of reinforcement of steel corrosion.
- Enrichment of starch with nanosilver particles allows for the obtaining of admixtures with additional properties (e.g., microbicidal) while maintaining increased resistance to corrosion in the reinforcing steel (if added to cross-linked starches).
- The research showed a positive effect of cross-linked starches stabilised with nanosilver on the passivation of reinforcing steel in cement composites, which means that the created admixture may additionally have microbicidal properties.
- The results are found to be an enabler for further full-scale testing with the use of 20 x 20 x 50 cm. In the main reinforced concrete elements, a different measurement procedure will be used. It is expected

that one of three main methods will be used, i.e. the linear polarisation resistance (LPR) method, the electrochemical impedance spectroscopy (EIS) method, or the galvanostatic pulse (GP) method. What is also important is that all of these methods can also be used for the "in situ" testing of large reinforced concrete structures.

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