Theoretical and practical aspects of improving the durability of steel reinforcement in transport designs, using passivation and plasticizing chemical additives

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Abstract. The article deals with the problem of steel reinforcement corrosion in reinforced concrete structures exposed to aggressive media, in particular in reinforced concrete construction of transport infrastructure, in snowy areas, and subject to the influence of chlorides contained in applied deicing agents. Basic schemes for preventing the reinforcement corrosion in reinforced-concrete structures have been considered and analyzed. Prospects of primary protection against corrosion of reinforcement by introducing chemical additives with plasticizing/passivating action in a concrete mixture with mixing water have been considered in detail. The physical/chemical mechanism of the protective action of a superplasticizer together with a passivator has been highlighted.

1. Introduction.
Deicing agents having in its composition chlorine ions, are widely used for deicing of roads in different countries. Chlorine ions adversely affect the reinforcement of concrete artificial structures in transport. The use of plasticizing additives together with oxidizing chemical additives, in an alkaline concrete system, tends to increase the steel reinforcement durability in structures of the transport infrastructure.

Problem definition. Globally, the corrosion of metals incurs huge losses, the global cost is $ 2.5 trillion, equivalent to 3.4% of world gross domestic product (GDP) for 2013 [1]. The proportion of reinforcement in the whole variety of metal products is not great, but its corrosion in reinforced concrete structures leads to gradual destruction of designs themselves, and subsequently to their costly repairs. In 1993, the United States spent 20 billion dollars on the repair of reinforced concrete bridges only because of the impact of chlorides [2]. Today, in the US, the repair costs because of reinforcement corrosion after exposure to deicing reactants are estimated at 325 million - 1 billion dollars a year [3]. The problem is global in nature.

Transport structures operate in different climatic regions: these are areas subject to periodic changes in temperature; sea areas where the air contains salt - metal corrosion activators; industrial areas with high humidity and aggressive towards metals, gases (CO₂, SO₂, NO₂, and others), snow-covered areas where deicing materials containing chlorides in their composition, are used. In addition to the environmental conditions, structures in the transport are subject to constant dynamic loads. Taken together, these factors lead to varying degrees of wear and tear of the protective layer of concrete structures used in transport. No matter how solid the concrete structure is, its unsoundness, over time, increases and corrosion of concrete is only growing, followed by the increases of metal reinforcement corrosion.
Aggressive ions getting on the exposed surface of a concrete structure, diffuse through the thickness of the protective layer to reinforcement, activating its corrosion. From all kinds of aggressions, the most destructive, and large-scale ones are of the chlorides causing defects whose elimination requires a lot of money and time costs.

2. Results and discussion.

Many ways to solve these problems have been proposed, studied and tested. However, a perfect solution is still not found, so far. Some effective methods for solving this problem include the following: increasing the thickness of the protective layer, the reduction of w/c ratio, increasing the density and impermeability of concrete, use of polymer-modified compositions, waterproofing of concrete surfaces, coating the surface of the reinforcement with epoxy resins, zinc, etc. All the marked methods, to a greater or lesser extent, have an inhibitory effect, but their long-term effectiveness is questioned [4]. At the stage of repair of reinforced concrete structures, migrating corrosion inhibitors are applied for steel reinforcement in concrete. For more than four years of testing, it has been found that such inhibitors are not effective for reducing the rate of corrosion, but, when tested some of them, there is a delay in the corrosion initiation at the penetration of chlorides [5]. Thus, the problem of developing an effective system to prevent corrosion, which will protect reinforcement steel, if not for all exploitation period, then at least for long time, is important.

The tendency to increase the durability of reinforcement steel in concrete under the influence of aggressive is evident at using chemical additives with passivation and plasticizing action, in concrete. Sodium nitrite (NaNO₂) tends to retain steel in a passive state, in the presence of chloride ions [6]. Sodium nitrite, in addition to the direct protection from steel reinforcement corrosion, has concomitant advantages, such as increasing the protective properties of concrete at strong carbonation of cement stone, increasing the concrete impermeability, its availability and economic profitability. The protection of concrete steel reinforcement with sodium nitrite lies in the fact that NO⁻₂ ions are adsorbed on the anode surface, reducing Gibbs free energy of the system and making difficult the transition of metal-ion atoms from a crystal lattice to the solution of [7]. The inhibitory ability of sodium nitrite, depending on the composition type and aggressive environment exposure time, is estimated at max. 80%.

Chemical additives plasticizing a concrete mixture – superplasticizers - based on naphthalene formaldehyde compounds do not show the inhibition ability in relation to the steel reinforcement exposed to chlorides. With the introduction of superplasticizer C-3 in the dosages of 0.5 … 0.7% of binder weight, recommended for plasticizing of a concrete mixture, there is a deterioration of protective properties in relation to reinforcement steel for which the aforesaid additives are not applied. The use of more effective additives, concrete mixture superplasticizers of third-generation, based of polycarboxylate ethers, also showed no significant positive effect, i.e. no significant inhibition of reinforcing steel in concrete exposed to aggressive environments. Superplasticizers significantly increase the density of concrete structures, putting off the time of the corrosion initiation, but when chlorides get on the reinforcement surface, the corrosion is inevitably activated.

At simultaneous introducing the passivating/plasticizing additives into the concrete mixture with mixing water, a synergy of their action was observed in certain cases. The results of the first systematic studies of the synergistic action of mixtures of inhibitors are described in [8].

At introducing sodium nitrite and superplasticizer based on naphthalene formaldehyde compounds (C-3) in the recommended dosages the synergy of their action was not observed, but by adding thereto a third component in the form of surfactant the inhibition ability was evaluated as very high (92%) [8]. Two surfactants different by nature, competed in adsorption on clinker minerals, which resulted in a sufficient amount of surfactant retained in the liquid phase, with fixing a film on the reinforcement surface, formed by the action of sodium nitrite.

In the scope of this work, two types of complex additives for the concrete mixture have been studied to improve the steel reinforcement safety in relation to structures for transport construction, based on sodium nitrite chlorides in different concentrations. In the first case, sodium nitrite was used in combination with the superplasticizer based on naphthalene formaldehyde (C-3) in excessive
concentrations, since at its recommended dosage the protective effect is not observed because of its high rate and degree of adsorption [9]. In the second case, together with sodium nitrite, a superplasticizer based on polycarboxylate ethers (DEGASETPC 7555) was used, at a concentration recommended by the manufacturer, as the polycarboxylate additives show lesser adsorption activity because of the presence of a large number of ionized groups in their structure, and differences in the properties of COONa- and SO3Na-groups [10]. The process of adsorption mechanism of polycarboxylate superplasticizer (PCE) is somewhat different than the one of the C-3. In aqueous solution, a COONa group dissociates into COO- and Na+, with forming a long chain group of anions. While considering the valences of calcium cations and COO- anions, the reaction stoichiometry is as follows: (surface cation Ca2+): an elementary surfactant unit equalling 1:2. Two polymer molecules (PCE) covalently bind to calcium cations, and the latter are subsequently incorporated into the crystal lattice of calcium aluminate hydrate. The represented interaction occurs at high polymer charge density, and therefore it is possible to make an assumption about the reason why carboxylic superplasticizers have a lower degree of adsorption than naphthalene sulfonates do. Obviously, this is because the energy of the sulfite – anions bond with calcium cations, is higher than that of COO- anions as their valencies differ twofold. Two COO- particles to calcium cation, are diametrically arranged in relation to each other. This is due to the interatomic distance between anions, resulting in weaker two separate one-electron bonds.

As a corrosion activator of steel reinforcement calcium chloride in amount 3% of cement, with mixing water, was used. Concrete extracts were preserved for 5 months, then within a month they were alternately wetted and dried. At the age of 6 months, anodic polarization curves were recorded by means of an accelerated electrochemical method using a potentiostat. In automatic mode, the sample was polarized by measuring the value of current in every 50-100 mV of potential change, and on base of the data obtained anodic polarization curve was plotted. The corrosion state of reinforcing steel in concrete was assessed by the current density and the potential drop in 60 seconds after turning off the power in accordance with the GOST 31383 [11].

Table 1. Improving the durability of steel reinforcement

| Z   | additive | Conc, % m.v. | Current density at the potential +300 mV, μA/cm² | Potential in (60±5)s after switching off the power, mV | Visually                                      |
|-----|----------|-------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|
| 1   | DEGASET PC 7555 | C-3       | 64.0                                           | -380…-280                                      | Corrosion pits, rust spots at the edge, spots in all the surface of size up to 20x15 mm, 40% |
|     |          | NaNO₂     |                                               | +70…+49                                       | Rebar clean                                   |
|     | 0.4      | CaCl₂     | 0.4…13                                        | 0                                               |                                              |
|     | 1.5      |           | 1.0…14.0                                       | -230…+50                                       | Rust film at the edge, a spot - 15x10 mm, one sample – no corrosion |
| A   | 0.5      | 3         | 18.3                                           | -380                                           | Corrosion pits, rust spots at the edge, spots in all the surface of size up 20x15 mm, 50% |
| 2   |          |           | 0.5…3.6                                        | -140…-20                                       | Separate rust spots in all the surface up to 30% |
| B   | 0.5      | 3         | 2…3.6                                          | -230…-80                                       | Corrosion pits, rust spots at the edge, spots in all the surface of size up to 15x10 mm, separate spots 30x25 mm, 30% |
|     | 1.5      |           | 4.4…14                                         | -230…-80                                       |                                              |

*Current density up to 10 μA/cm² inclusive at the potential +300 mV attests to passive state of reinforcement

**Potential over +5 mV in (60±5)s after switching off the current, mV attests to passive state of reinforcement

The protective action of the sample 1B (Table 1) is due to the chemisorption of nitrite ion on the positively charged steel surface, followed by the formation of an oxide film in a complex system of processes. A simultaneously introduced surfactant is mainly adsorbed on the aluminate phases of cement.
clinker also due to the increase of the adsorbent specific surface area due to the formation of high disperse hydroaluminates causing intense absorption of the additive from the solution. C-3 binds with clinker minerals primarily as chemosorption bond, namely superplasticizer molecules covalently join with additional Ca\(^{2+}\) cations, which are built in an initial stage in the formation of crystalline lattice structure of hydroaluminates and calcium hydrosilicates. The covalent bond indicates the irrevocable adsorption of plasticizer molecules. On the clinker minerals a monolayer of organic-phase is formed, and surfactant adsorption is terminated. Not adsorbed molecules are in a free state in the liquid phase. At the moment of contact of concrete mixture with reinforcement free surfactant molecules are adsorbed on its surface, displacing chlorides and helping to strengthen the passive film upon sodium nitrite. It should be noted that metals such as iron, have greater adsorptivity than minerals that make concrete composition [12].

3. Conclusions.
The samples 1B showed complete absence of corrosion and that confirms the trend of increasing the durability of steel bars due to using the passivating/plasticizing action additives, under the influence of chlorides.

However, the full realization of such protection of steel reinforcement, including in structures for transport construction, often exploited in rough aggressive conditions, adsorptive interactions of plasticizing additives with concrete components should be considered. Based on the investigations performed it can be concluded that by using a complex additives comprising a mixture of sodium nitrite inhibitor and surfactants, in concrete their protective capacity with respect to the steel reinforcement is the higher, the lower the adsorption of these surfactants on cement minerals is.

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