

Assessment of Passivating Properties of Composite Binder Relative to Reinforcing Steel

Valeriy Stanislavovich Lesovik, Nataliya Ivanovna Alfimova, Aleksey Vladimirovich Savin, Aleksandr Vladimirovich Ginzburg and Nikolai Nikolaevich Shapovalov

Belgorod State Technological University named after V.G. Shukhov,
Belgorod, Kostyukov Street, 46, 308012, Russia

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Abstract: Due to the fact that at the present environmentally friendly technologies are becoming the most urgent, we observe re-orientation of building materials industry towards concrete with low cement consumption. One of the innovative materials which allow to create such concretes are composite binders (CB). However, there are a number of reasons which slow down their widespread use, in particular for manufacture of reinforced concrete products, one of which is insufficient knowledge about CB influence upon the processes of tension reinforcement corrosion. In the composite binding agents a part of clinker component is replaced by silica-containing component, which is activated during the milling process, takes part in hydration processes, binding hydrated calcium silicate, which in turn contributes to reducing the alkalinity of the medium and as a result, may have a negative effect on the passivating concrete characteristics with respect to reinforcing. In this connection the ability of composite binders made with quartz sand of sedimentary origin and quartzite sandstone with green schist metamorphism to passivate the reinforcing steel have been studied. Analysis of the current density of steel, steel stationary potential and pH indicate that composite binders under investigation have the original protective property with respect to the reinforcing steel. A greater importance is given to the total binder consumption rate as well as the presence of superplasticizer.

Key words: Corrosion • Concrete • Reinforced concrete • Composite binders • pH • Anodic polarization curves

INTRODUCTION

At present, using the most environmentally friendly technologies has become an urgent trend in construction, the essence of these technologies is to reduce the energy costs of production, improve the quality of the final product, use of technogenic raw materials, etc. The written sources commonly refer to terms like "green concrete" and "green building". In the U.S. and Europe they are such types of concretes, in which the cement consumption is reduced by 50-60 %. The enterprises engaged in the production of this type of concrete have significant tax concessions [1, 2].

Composite binders (CB) may be regarded as innovative materials as well. They can form the basis for creation of "green concrete": fine-ground multi-component cement (FGMC) and low water demand binder

(LWDB), in which 10 to 70 % of clinker component can be replaced by siliceous raw materials of both natural and technogenic origin [3-5].

Application of composite binding results in the change in microstructure as well as composition of new formations. This reduces not only the capillary porosity, but also the size of new formations, the composition of the calcium hydrosilicate is changed resulting in fewer microcracks during solidification of the system [6, 7]. It is established that as a raw material for producing CB it is reasonable to apply certain types of rocks. From the rocks of magmatic origin-volcanic with glassy structure; metamorphic-quartz-bearing rocks of greenschist metamorphism, sedimentary-silicites zone of diagenesis, early catagenesis and others [8, 9]. It made it possible to develop a wide range of composite binders, with the use of materials of different origin [4, 9, 10].

However, it should be noted in the production of reinforced concrete products this kind of has not found wide application. This is primarily due to the fact that the issues of the corrosion behavior of reinforcing steel in concrete using TMC and LWDB in which the proportion of clinker component is less than 50% has not been sufficiently studied.

Corrosion resistance and durability of concrete structures made on composite binding is a major problem, the solution of which is aimed at increasing the service life of buildings and structures of various purposes. According to different statistical estimates from 15 to 75% of structures are exposed to corrosive media and about 30% of them need protection. In addition, various expert estimate that from 5 to 10% of building structures become out of commission annually.

The theory of corrosion and protection of reinforcement in concrete structures was developed in the works V. Moskvina, S.N. Alekseev, V.S. Artamonov, V.I. Grandma, Y.M. Bazhenov, F.M. Ivanov, N.K. Rosenthal and others. Out of foreign scientists Kishitani, Chalon, Shteltseya and others are also known as well as works concerning the issues of corrosion resistance of reinforcing steel in concrete mixed based on mixed binding agents [10, 11].

However, the issues of quality and durability of building structures, both in technical and economic aspects are attracting more and more attention from construction specialists. It is evident that in many cases the increase of initial costs spent on manufacturing the structures and their protection seems economically reasonable if it allows to reduce the number and cost of repair works during the service period. This applies particularly to reinforced concrete structures made on CB, in which the steel reinforcement may be well protected with concrete and the latter can be given considerable resistance in conditions of alternate freezing and melting, wetting and drying.

As it is known, steel corrosion rate in concrete depends on the aggressiveness of water which is the medium, which in this case can be measured by pH and oxygen content. Long-term stability of steel in dense cement concrete is provided by passivity of iron in alkaline electrolytes, the alkalinity of which should have $\text{pH} = 11,8$.

The passive film on the steel is destroyed with lowering pH of concrete pore liquid, for instance, due to its carbonation, presence of active admixtures in the concrete which neutralize calcium hydroxide, as well as the presence (in amounts above critical value) chlorides and

sulphates. Based on the fact that composite binders includes siliceous component which binds calcium hydroxide to form additional low basic hydrosilicates, we can assume that, along with hardening of the concrete structure, reducing the alkalinity of its liquid phase is initiated. This, in turn, can reduce passivating properties of the concrete on CB relative to the steel reinforcement. In this connection, the aim of this research was to identify abilities of composite binders to initially passivate the steel reinforcement.

Methodology: Methods of establishment of potentiodynamic polarization curves, the essence of which is based on the assessment of passivating action of concrete on steel reinforcement and produce electrical current density dependence on the electrical potential of steel reinforcement (potentiodynamic method) or the value of the potential of steel reinforcement in concrete from the current density (half-cell method) and comparing the results with critical values established.

When steel electrode is immersed into electrolyte solution, iron ions pass into the solution (anodic process). An equivalent amount of electrons is released in the metal. Electric double layer is formed on "metal" - "liquid" edge, blocking further dissolution of the metal. Excess electrons, in turn, deoxidize depolarizer ions (cathodic process), the equilibrium is disturbed in the double layer, and an amount of iron ions pass into the solution again. If a concrete sample with embedded steel electrode is immersed into the electrolyte and switch into a circuit, then, maintaining a certain potential value, it is possible to observe the change of current in the circuit, i.e. the speed of electrochemical process (potentiostatic method). The polarization curve "current-potential" characterizes the dependence of the rate of electrochemical processes at the electrode surface on the potential imposed by an external power source.

In case a sample is exposed to each potential value selected to current stabilization, we obtain a potentiodynamic curve. With the increase in density of current flowing through the electrode, potential of the cathode becomes more negative compared to initial value and the potential of the anode - more positive. Offset potential with changing current characterizes polarizability of the electrode-cathode or anode respectively. According to the degree of electrode polarizability we can judge on the corrosion flow rate. If the polarizability of the electrode is not significant, then the slowdown of the corrosion process is insufficient. When a slight increase in current is accompanied by a significant shift of

potential-this testifies to the fact that the corrosion process is strongly retarded. For the test in suspensions of composite binders paste of normal consistency were prepared.

A rod, decontaminated and degreased with acetone was immersed into suspension and the anodically polarized. Then, the area of corrosive damage was determined.

Basic Part: The following was used during the research as binders: fine ground blended cements and binders with low water consumption with the use of crushing screenings quartzite sandstone from Lebedinski mining concentrator (FGC-50 (DPC), BLWC-50 (DPC)) and quartz sand (FGC-50 (P), BLWC-50 (R)), as well as Portland cement CEM I 42,5 N manufactured at Belgorod cement factory (control composition). "Polyplast SP-1" admixture in the amount of 0.7% by weight of cement was used as a superplasticizer for obtaining a binder with low water consumption. Making composite binders was carried out by joint milling of all components in a laboratory ball mill until the specific surface area reached 500 m²/kg. This manufacturing method allows to activate not only the clinker component in Portland cement, but additionally increase the activity of silica component due to its partial amorphisation.

For test solutions were prepared on pure composite binders (without admixtures), as well as solutions of binders to sand in the ratio of 1:2 and 1:3 by weight.

The anodic polarization curves were traced immediately after heat and humidity treatment (in the regime of 3+6+3 at t = 80 °C) and then after six months of alternate wetting and drying. This was reasoned by the fact that concretes based on binders, made with siliceous components are most rationally used after steaming, in addition, protective properties of concrete after heat treatment are worse compared to concrete, which hardens under normal conditions.

According to ST SEV 4421-83 the criterion for evaluating the protective effect of concrete in relation to steel reinforcement is the current density at a potential of +300 mV.

As the data indicated in Table 1, Figure 1 show, current density value in steel does not fall below critical-10 mA/cm², at the same time, the value at the stationary potential of all composite binders in the initial state does not exceed-400 mV, it means that the CB under investigation possess the original protective property against steel reinforcement.

Table 1: Test Results for steel condition pastes and sand solutions based on composite binders

Type of binder	Binder to sand ratio	Steady-state potential, E _{st} , mV		Current density at E=+300 mV, i _E =300mA/Åm ²		Corrosion area S, %		pH value	
		original state		original state		original state		original state	
		6 month tests	6 month tests	6 month tests	6 month tests	6 month tests	6 month tests	6 month tests	6 month tests
CEM I 42,5H	Pure binder	-260	-280	6,4	4,8	0	0	12,46	12,33
	1:2	-340	-120	4,5	3,2	0	0	12,28	12,18
	1:3	-310	-80	7,7	2,7	0	0	12,25	12,14
CEM I 42,5H + ÑP1	Pure binder	-210	-180	6,3	3,3	0	0	12,57	12,43
	1:2	-290	-60	7,1	5,8	0	0	12,41	12,36
	1:3	-260	-40	3,4	1,8	0	0	12,22	12,18
FGC-50(Quartzite sandstone-50%-cement-50%)	Pure binder	-230	-420	8,5	6,2	0	0	12,32	12,16
	1:2	-210	-58	5,7	4,2	0	0	12,28	12,07
	1:3	-180	-120	3,8	2,4	0	0	12,18	11,98
LWCB-50 (Quartzite sandstone-QSS)	Pure binder	-220	-380	9,1	11,3	0	0	12,18	12,11
	1:2	-280	-240	7,0	1,8	0	0	12,08	12,01
	1:3	-180	-220	5,5	2,7	0	0	12,05	11,97
FGC-50 (S)	Pure binder	-350	-260	7,8	7,1	0	0	12,18	12,06
	1:2	-360	-380	7,3	4,6	0	0	12,11	12,01
	1:3	-280	-110	5,7	3,5	0	0	12,03	11,96
LWCB-50(S)	Pure binder	-380	-440	4,4	2,7	0	0	12,24	12,11
	1:2	-200	-360	5,1	5,3	0	0	12,13	12,0
	1:3	-190	-380	7,2	4,5	0	0	12,01	11,91

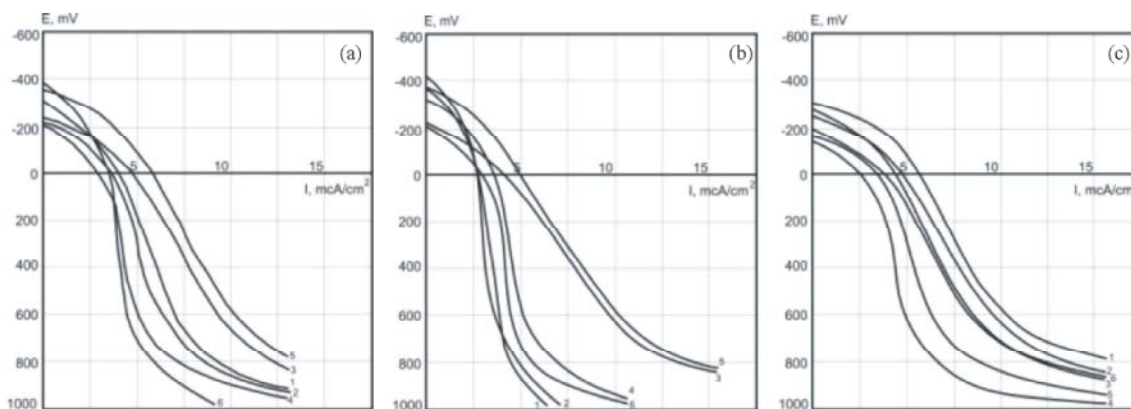


Fig. 1: Anodic polarization curves of steel in hardened cement paste based on composite binders, original state: α -pure binder; b-binder: sand (1:2); c-binder: sand (1:3) 1-CEM I 42,5H; 2-CEM I 42,5H + SP1; 3-FGC-50 (QSS); 4-LWCB-50 (QSS); 5-FGC-50 (S); 6-LWCB-50 (S)

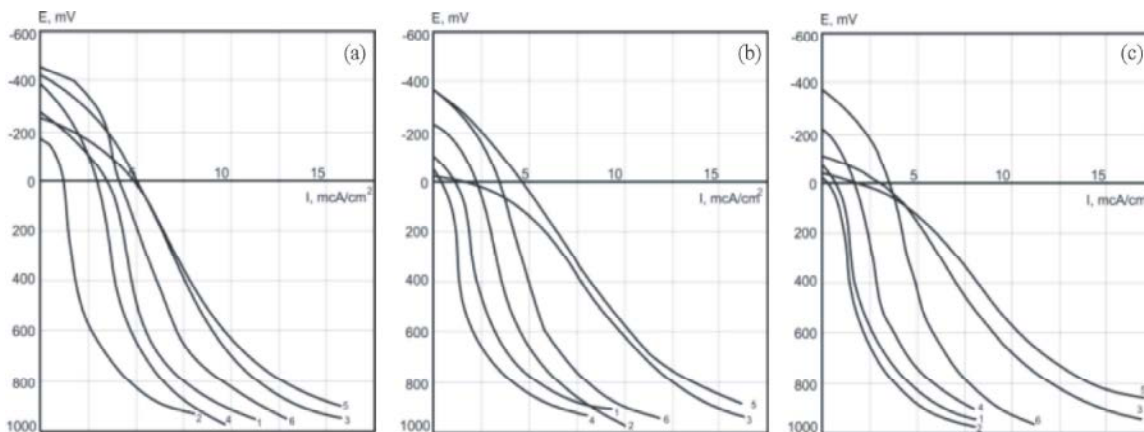


Fig. 2: Anodic polarization curves of steel in hardened cement paste based on composite binders, after 6 months: α -pure binder; b-binder: sand (1:2); c-binder: sand (1:3) 1-CEM I 42,5H; 2-CEM I 42,5H + SP1; 3-FGC-50 (QSS); 4-LWCB-50 (QSS); 5-FGC-50 (S); 6-LWCB-50 (S)

It should be noted that values of current density of steel for low water consumption binders are lower compared to fine grain blended cements because of greater density of the protective layer, created by low water consumption binders. This conclusion is confirmed by the studying the microstructure of sample composite binders, according to which a FGC-50 among non-hydrated cementing mass we observe grains of non-hydrated clinker minerals, dispersion degree of which reaches 100-200 μm , the predominant size of admixtures being 50-80 μm . Grains of sand, generally have the following dimensions-up to 50 μm , grain sized 100-150 μm . While LWCB-50 is characterized by a homogeneous, compact and finely dispersed structure, due to the introduction of superplasticizer into a system, which improves the grinding processes.

pH values of composite binders are slightly below that of Portland cement, however they are within the range providing steel passivity (over 11.80). In this case, steel corrosion damage in composite binders is not observed. It should be noted that with the increase in fine aggregate consumption in the mixture, pH decrease is observed, this regularity also lasting after 6 months testing (Table 1) (Fig. 2).

CONCLUSION

Thus, while selecting concrete composition, composite binder consumption will be essential. The quantity of CB in the mixture should provide pH values, not below critical values, which ensure passivity of steel.

Conclusions: In general, the analysis of the data showed that composite binders under investigation made with quartz sand and quartzite sandstone crushing screenings have initial barrier properties to the steel reinforcement, as confirmed by the current density in steel and stationary potential. At the same time great importance is given to overall consumption of binder in the mixture which decreases with decreasing pH, which may become the main cause of corrosion of the reinforcement.

To increase protective properties of composite binders may also be due to introduction of grinding superplasticizer which optimizes granulometry of binders, which has a positive effect on the structure of the cement paste, the density of the protective layer and therefore the corrosion resistance of the reinforcement.

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