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STABILITY OF POLYMER SULFUR CONCRETE WITH STEEL REINFORCEMENT

***Jurij Orlowski*[1], *Mariusz Leszczewski*[1], *Igor Margal*[2]**
[1]Faculty of Technical Sciences
Uniwersity of Warmia and Mazury, Olsztyn
[2]University of Lvovska Politechnika, Lvov, Ukraine

Key words: Concrete, corrosion of steel, reinforcement, sulfur concrete.

Abstract

Corrosion resistance of steel reinforcement in sulfur concrete depends on its structure density, presence of sulfur compounds in concrete components, humidity of medium.

On the basis of potentiostatic investigations and corrosive tests, the following recommendations were made. It is necessary to control the contents of hydrogen sulfide, organic impurities and acids (recalculated for sulfuric acid), as specified in relevant standards for industrial sulfur, to assure the passivating effect of sulfur concrete on steel reinforcement. Fly ash from heating-and-power plants used as a filler, productive waste of sulfur used as a binder and filler must not contain more than 3% of water soluble sulfates (recalculated for SO_3). These requirements, recommended in standards, regulate the quality of materials used for producing sulfur cement and sulfur concrete.

In order to improve the protective properties of sulfur concrete as regards steel reinforcement it is necessary to develop compounds with optimum density, strictly observing technological regulations in the manufacturing process. Concrete structure must be faultless. Adequate reinforcement adhesion to concrete and density of their contact zone are also of primary importance.

TRWAŁOŚĆ BETONU SIARKOWEGO ZBROJONEGO STALĄ

***Jurij Orlowski*[1], *Mariusz Leszczewski*[1], *Igor Margal*[2]**
[1]Wydział Nauk Technicznych
Uniwersytet Warmińsko-Mazurski, Olsztyn
[2]Uniwerytet, Lwowska Politechnika, Lwów, Ukraina

Słowa kluczowe: beton, korozja stali, zbrojenie, beton siarkowy.

Streszczenie

Odporność korozyjna zbrojenia w betonie siarkowym zależy od jego struktury, obecności związków siarki w składnikach betonu, wilgotności środowiska. Na podstawie badań potencjostatycznych i testów korozyjnych sporządzono następujące zalecenia. Aby zapewnić wpływ pasywacyjny betonu siarkowego na zbrojenie stalowe, należy sprawować kontrolę zawartości siarkowodoru, zanieczyszczeń organicznych i kwasów (w przeliczeniu na kwas siarkowy) określonych normami dla siarki przemysłowej. Popiół lotny z elektrowni używany jako napełniacz oraz odpad produkcyjny siarki używany jako spoiwo i napełniacz nie mogą zawierać więcej niż 3% rozpuszczalnych w wodzie siarczanów (w przeliczeniu na SO_3). Te wymogi, zalecane w normie, regulują jakość materiałów stosowanych do wytworzenia cementu i betonu siarkowego.

Aby zwiększyć właściwości ochronne betonu siarkowego wobec stali zbrojeniowej, należy tworzyć związki o optymalnej gęstości i ściśle przestrzegać norm technologicznych w procesie produkcyjnym. Struktura betonu musi być wolna od uszkodzeń czy wad, bardzo istotna jest także odpowiednia adhezja betonu do zbrojenia, a zwłaszcza gęstość ich strefy kontaktu.

Introduction

The passivating effect of concrete on steel reinforcement is the foundation of its protection against corrosion. Our experience and investigations show that the duration of ordinary concrete passivating effect depends mainly on its density and thickness of the reinforcement protective coating (MOSKVIN et al. 1980).

Capillary and porous structure of cement concretes presupposes their inevitable interaction with medium. In ordinary, dense-structure concrete on portland cement steel is passive owing to saturation of cement stone porous liquid with calcium oxide hydrates, whose pH is 12–12.5.

A reduction in the pH of the liquid phase in the process of accumulation of depassivator ions, resulting from the aggressive medium effect, leads to the processes of reinforcement corrosion.

Mechanism of reinforcement corrosion in sulfur concrete is qualitatively different from that observed in cement concrete. The absence of capillary and porous structure in sulfur concrete limits to a great extent its interaction with the surrounding medium. Cement concrete is characterized by an alkaline medium, sulfur concrete is characterized by a neutral one, and, under constant effect of water – by a subacid one. With technological defects and destructive processes there appears a serious threat of steel reinforcement intensive corrosion.

Data on steel reinforcement preservation in sulfur concrete are not numerous, and their nature is contradictory. Thus, according to the data (VROOM 1976), signs of reinforcement corrosion in have not been found in products made of sulfur concrete, kept for 2 years in the open, which can be explained by low concrete air and water permeability. According to (SWAMY, JURJEES 1986), considerable corrosion of reinforcement has been observed while storing beams with steel reinforcement. When analogous beams, but made of modified sulfur concrete were stored in water, the passivating effect of concrete as regards reinforcement has been noted.

An analysis of the results obtained (Swamy, Jurjees 1986) allows to assume that the reason for reinforcement corrosion is rather its composition with ash dust as a filler (fly ash from heating-and-power plants) than poor passivating properties of sulfur concrete. Fly ash is known to contain various sulfurous compounds, greatly increasing the danger of corrosion for reinforcement under a continuous effect of water. Substitution of silica flour by fly ash in cement concretes is also known to reduce the pH of porous liquid, to increase porousness and permeability of concrete structure (Yakub, Alekseev 1971). Proceeding from modern views, the state of reinforcement in concrete can be influenced by ions H_2S^-, SO_4^{-2} , S^{-2} and atomic hydrogen. Investigation of hydrogen sulfide corrosion reveals multiple acceleration of corrosion in moist medium in the presence of hydrogen sulfide. It results not only in general corrosion acceleration, but in distinctively revealed tendency of reinforced steel to become brittle, which results from the fact that atomic hydrogen reacting with metal penetrates into steel structure, recombines into molecular hydrogen and creates very high pressures.

Information on the effect of elementary sulfur on steel corrosion in concrete is not available. But according to the data of former Institute of Sulfur (Lvov), autoclave sulfur and sulfur from underground smelting contain 2–5 g/t of hydrogen sulfide, content of organic impurities leading to extra formation of hydrogen sulfide and solid carbon bisulfide complexes, which may be the reason for unstable passive state of steel. Sulfur-containing wastes, such as, for example, bottom ash, used as adhesive for sulfur concrete manufacturing (Orlovsky 1990) contain even greater amounts of these compounds.

Materials and Methods

The aims of the investigation were to study reinforcement preservation and to determine the rate of steel reinforcement corrosion in sulfur concrete. Samples were exposed to air-dry conditions and stored in water for 360 days. Sulfur concrete was the subject of research (Table 1).

Chemically pure sulfur, technical sulfur modified by 5% of dicyclopentadiene (DCPD) and productive waste of sulfur containing 51.2% of elementary sulfur were used as adhesive. The content of organic impurities accounted for 0.62%, acids recalculated for sulfuric acid – 0.04%, hydrogen sulfide – 0.017%, 4 times exceeding acceptable standard values for technical sulfur.

Productive waste of sulfur is a by-product containing waste of sulfur. It`s being manufactured by its underground smelting and further purification.

Table 1

Composition and characteristic of concretes

Series	Kind of Filler	Specific Surface of Filler, m^2/kg	Content, mass %				Strength, MPa	
			sulfur	filler	sand	chips	compres-sion	bending Tension
SC I	Silica Flour	350	13	13	24	50	49.2	10.9
SC II	Fly Ash	320	13	13	24	50	42.3	8.0
SC III	Productive Waste of Sulfur	–	26	–	24	50	35.1	6.8
SC IV	Fly Ash	320	13	13	24	50	65.3	19.5

The chemical composition of waste was as follows (mass per cent): sulfur – 51.2, SiO_2 – 2.5, $A1_2O_3$ – 0.21, Fe_2O_3 – 0.24, CaO – 22.3, MgO – 0.04, CO_2 – 16.8, SO_3 – 0.9 organic impurities – 5.81. Acid content recalculated for sulfuric acid was 0.05%, with hydrogen sulfide content of 0.051 brought about during testing. The initial content of hydrogen sulfide in fly ash was 0.0035%.

Sulfur modifier has been chosen for the following reasons. According to foreign publications, carboniferous dicyclopentadiene $C_{10}H_{12}$ obtained from crude benzol fraction treatment is most frequently used as plasticizer and inhibitor of sulfur polymer state. It is connected with its temperature combinability with sulfur, its ability of interpolymerization, its uninflammable properties, low cost, as compared with the other modifiers. The process of sulfur modification by DCPD was considered in paper (ORLOVSKY 1992).

Silica flour and fly ash from heating-and-power plants with a specific surface 350 and 320 m^2/kg correspondingly were used as fillers. The content of sulfur compounds in fly ash recalculated for SO_3 was 3.1, and the content of organic impurities – 2.1 (mass %). Quartz ravine sand (size modulus 1.4, content of clay particles 2.5%) was used as fine aggregate, and 5–10 mm granite chips were used as coarse aggregate. Chemical and granulometric compositions of fillers are given in Tables 2 and 3.

Table 2

Chemical composition of fillers (%)

Filler	SiO_2	Al_2O_3	Fe_2O_3	CaO+MgO	Na_2O+K_2O	SO_3	Calcination Losses
Silica Flour	95.60	2.88	0.39	0.32	–	–	0.81
Fly Ash	49.00	27.50	12.50	3.80	2.10	3.10	2.10

Table 3

Granulometric composition of fillers

Filler	Content, % of fraction particles, μm					
	2 and <	2 – 5	5– 10	10 – 30	30 – 50	100 and >
Silica Flour	3.60	6.45	27.60	18.70	11.30	32.40
Fly Ash	2.50	7.05	22.40	20.80	14.10	33.20

The size of the samples for corrosion tests was 4 x 4 x 16 cm, with bars 8 mm in diameter and 100 mm long, made of A II grade 5 steel concreted in the center, grinded to the 7th grade. For potentiostatic investigations cylindrical samples 50 mm in diameter and 80 mm high were produced.

There were three samples for corrosion tests for each period of exposure. At the end of exposure the samples were broken along the reinforcement rod and the state of reinforcement was estimated.

The difference between the initial and final mass of bars after pickling with a 10% solution of hydrochloric acid characterized their mass loss. This value provides quantitative presentation of corrosion losses and can be used for determining both velocity and intensity of the corrosion process in $g/m^2 \cdot h$ by the formula:

$$V = \Delta P \,/\, F \cdot \tau,$$

where

ΔP – mass loss, g,

F – total surface area of reinforcing bar, m^2,

τ – period of testing, hours.

The passivating properties of sulfur concrete were simultaneously studied by an electromechanical (potentiostatic) method by plotting polarization curves with the help of a potentiostat at the rate of potential superposition 0.6 mV/s, determining current density. An impregnated calomel electrode was used as a reference electrode, and a platinum electrode – as an auxiliary one.

The investigation was carried out with cylindrical samples 50 mm in diameter and 80 mm high. A metal bar made of thermally reinforced steel of A_T – grade 6 with a 20 mm protective coating was used as reinforcement.

After placing the samples in the medium under study they were connected to a potentiostat for 1.5–2 hours, for stabilization of temperature and electrode reactions, then the value of stationary potential was measured without the superposition of potential from the outside. Afterwards a potential of about 1200 mV in the automatic mode was superimposed over the electrode with the help of a potentiostat, changing it at a rate of 2.4 V/hour and measuring the value of current every 50–100 mV (potentiodynamic method). The accuracy of maintaining the polarizing current on the potentiostat accounted for 0.5% of the established value. The error of voltage measurement on the scale of voltmeter was ±2% of the established value.

The results of investigations are presented in the form of charts in a coordinate system: current density – on *X* – axis, potential – on *Y* – axis.

The state of steel was estimated following the criteria suggested by the Research Institute of Reinforced Concrete, according to which steel in concrete is passive if current density does not exceed 10 mcA/cm^2 at a potential of 300 mV in a loaded calomel electrode. If it reaches a level of 10 to 25 – steel is in unstable passive state and corrosion is possible. Density exceeding 25 mcA/cm^2 enables intensive steel corrosion.

Results

Steel reinforcement corrosion, including the velocity and intensity of the corrosion process in sulfur concrete, is shown in Figure 1.

An analysis of the results proved the following. With chemically pure sulfur as adhesive and quartz flour (series SC I) as aggregate – test staff – with samples exposed both in water and under air-dry conditions of storing for 360 days there were no signs of reinforcement corrosion.

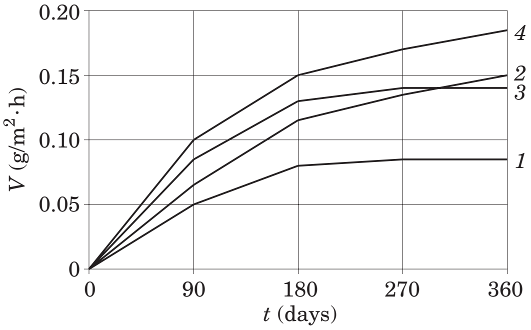

Fig. 1. Steel reinforcement corrosion velocity in sulfur concrete: *1* – samples of SC II series exposed under air-dry conditions, *2* – the same, in water, *3* – samples of SC III series under air-dry conditions, *4* – the same, in water

The samples produced using fly ash, technical sulfur (series SC II) and bottom ash (series SC III) showed signs of reinforcement corrosion on the 90th day of exposure, both under air-dry conditions and in water. Then corrosion velocity grew and, what's more, in water it was higher than when stored in air-dry conditions.

The samples produced using fly ash and technical sulfur, modified by dicyclopentadiene (series SC IV), showed no signs of reinforcement corrosion after 360 days of exposure under air-dry conditions. The samples stored in water had slight corrosion spots on after 360 days.

The anode polarization curves shown in Figure 2 allow to understand the electrochemical state of steel in concrete. Passive steel unlike active

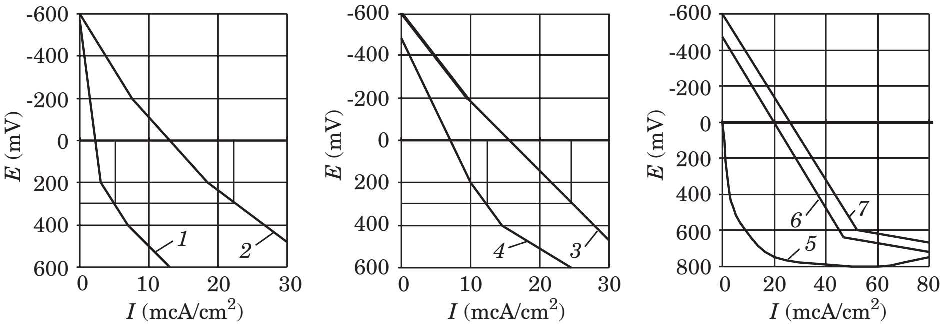

Fig. 2. Anode polarization curves of steel in aqueous extracts: *1* – sulfur concrete, series SC I, *2* – the same, series SC II, *3* – the same, series SC III, *4* – the same, series SC IV, *5* – portland cement at Na_2SO_4 concentration, g – eq/l from 0 to 0.001, *6* – the same, from 0.01 to 0.1, *7* – the same, from 0.5 to 1.0 (MOSKVIN et al. 1980)

steel is very polarized, i.e. its potential is shifted abruptly towards the positive end even at low density of current superimposed. At certain potential the curve becomes more sloping, which indicates the beginning of oxygen release (water electrolysis) or steel dissolution.

An analysis of anode polarization curves shows that steel in water-saturated samples of series SC I was in passive state, steel of series SC II, SC III and SC IV was in unstable passive state and, therefore, its corrosion was possible, this fact being corroborated by direct corrosion tests. Besides, the samples of series SC IV proved that losing reinforcement passive state is close to the stability criterion, i.e. current density of 12.5 mcA/cm^2 versus the standard of 10.

Sulfate – ions SO_4^{-2} are known to produce a considerable activating effect on steel. Anode polarization curves of steel in aqueous extracts from portland cement at different concentrations of sodium sulfate are given for comparison. Curves 5, 6 and 7 (Fig. 2) show that steel is passive in the extract without sulfate or with its small content. Steel activation begins at sulfate – ion content > 0.01 g-eq/1 (800–1000 mg/l), thus anode curves in an alkaline medium of cement stone will shift to the right with an increase in the sulfate ion content.

The greatest acceleration of steel corrosion by hydrogen sulfide takes place at its small concentration in the presence of oxygen. Sulfide sulfur in the process of oxidation in the presence of moisture apparently doesn't participate directly, but accelerates corrosion.

Ferrous steel that can be formed on the surface of steel in the presence of H_2S – is a non- polarized cathode with low potential and forms effective microgalvanic cell. Reaction $Fe^{-2} + H_2S \rightarrow FeS + 2H^+$ will shift abruptly to the right in alkaline medium and to the left - in sulfur concrete medium.

Summary and Discussion of Results

The results obtained indicate that the availability of hydrogen sulfide in sulfur from underground smelting, as well as the availability of sulfur compounds, in particular, water soluble sulfates, in fly ash and productive wastes of sulfur, have a decisive effect on corrosion resistance of steel protected by sulfur concrete. The availability of organic impurities in sulfur, fly ash and wastes, whose amount can increase in the process of sulfur storage and transportation, results in hydrogen sulfide formation. The availability of hydrogen sulfide in an aqueous medium accelerates corrosion processes in steel. In this case, to provide reliability of the passivating effect of sulfur concrete on steel reinforcement, the contents of hydrogen sulfide, organic impurities and acids (recalculated for sulfuric acid) must be reduced to values considered standard for technical sulfur, i.e. (mass part%): 0.04, 0.5 and 0.02 respectively. Fly ash from heating-and-power stations used as a filler and productive waste of sulfur used as a binder and filler must not contain more than 3% of water soluble sulfates (recalculated for SO_3). These requirements, recommended in relevant standards, regulate the quality of materials used for producing sulfur cement and sulfur concrete.

In order to improve the protective properties of sulfur concrete as regards steel reinforcement it is necessary to develop compounds with optimum density, strictly observing technological regulations in the manufacturing process, like in the case of cement concrete. Concrete structure must be faultless. Adequate reinforcement adhesion to concrete and density of their contact zone are also of primary importance.

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