# Protection of steel by environmentally friendly anti-corrosion pigment

Mariia-Olena Danyliak<sup>1</sup>, Ivan Zin<sup>1,2</sup>, Myroslav Holovchuk, Sergiy Korniy<sup>1</sup>

1. Karpenko Physico-Mechanical Institute of National Academy of Science of Ukraine, UKRAINE, Lviv,

5 Naukova str., E-mail: <u>danyliak-olena@ukr.net</u>

2. Lviv Polytechnic National University, UKRAINE, Lviv, 12 Stepan Bandery str.

Abstract – The corrosion resistance of 09G2S steel in 0.1% NaCl solution and in extracts of pigment based on zeolite and monocalcium phosphate was investigated. It was shown that pigment has an inhibitory effect for steel, and its efficiency is maximum at a mass ratio of zeolite and phosphate components 1 to 3.

Keywords - corrosion environment, steel, anticorrosion pigment, zeolite, monocalcium phosphate.

### Introduction

Mild steel is extensively used in the various fields of mechanical engineering, construction or power engineering. Mild steel is strength and relatively inexpensive, but is not corrosion resistant [1]. The electrochemical corrosion of steel is intensified in media contained chloride ions [2]. To corrosion protect of steel is using paint coatings containing anticorrosion pigments [3]. Today, the most common anticorrosion pigment is zinc orthophosphate and its other modifications [4]. However, its efficiency is not high due to its low solubility in water [5]. In [6] it was proposed to replace zinc phosphate with dicalcium phosphate, which has similar anticorrosion properties and lower cost.

The aim of the present work was to study the protective properties of an anticorrosion pigment based on zeolite and monocalcium phosphate by obtained mechanochemical method.

#### Materials and methods

The pigments were obtained by mechanochemical interaction of monocalcium phosphate in NaA-zeolite in a high-energy Retsch PM 100 planetary ball mill during 1 h. The rotational velocity of the mill cylinder was 200 rpm. The weight ratios of the grinding mixture of monocalcium phosphate and zeolite were 1:3; 1:1 and 3:1.

The corrosion resistance of the 09G2S steel was studied by potentiodynamic polarization method using MTech COR-500 potentiostat with a saturated Ag/AgCl reference electrode and an auxiliary platinum electrode. The potential scanning rate was 2 mV/sec. The area of working samples was 1 cm<sup>2</sup>. A 0.1% NaCl solution without and with 1 g/l of zeolite/calcium phosphate pigments served as a corrosive environment simulating rainfalls in the industrial atmosphere.

The morphology of pigments and steel surface after immersion in corrosive media was studied by using an EVO-40XVP scanning electron microscope with an INCA Energy-350 system.

#### **Results and Discussion**

In fig. 1 presented potentiodynamic polarization curves of steel in a 0.1% NaCl solution without and with extracts of zeolite/phosphate pigments at different ratios of the components. The electrochemical corrosion of steel proceeds under mixed control. The lowest corrosion-current density and, hence, the highest corrosion resistance of the metal were detected in a pigment extraction with the zeolite/phosphate ratio equal to 1:3. Moreover, the mechanochemically obtained zeolite-phosphate pigments inhibit corrosion more efficiently than their simple mixtures.



Fig. 1. Potentiodynamic polarization curves of 09Γ2C steel after 3 (*a*) and 24 h (*b*) immersion in 0.1% NaCl solution: 1 – without inhibitor; 2, 3, 4 – with pigments obtained by mechanochemical method at ratios of zeolite and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>:1: 3, 1: 1 and 3: 1, respectively; 5, 6, 7 – with simple mixture of zeolite and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> at weight ratios: 1: 3, 1: 1 and 3: 1, respectively. The pigments and mixture concentration was 1 g/l.

Table 1

Electrochemical characteristics of 09G2S steel after immersion in a 0.1% NaCl solution without and with zeolite– $Ca(H_2PO_4)_2$  pigment (1 g/l)

	Ratio of	Immersion, h						
Type of pigment	zeolite:		3	24				
	$Ca(H_2PO_4)_2$	E <sub>cor,</sub> V	$i_{\rm cor}$ , mA/cm <sup>2</sup>	E <sub>cor</sub> , V	$i_{\rm cor}$ , mA/cm <sup>2</sup>			
Without pig	-0,55	7,0·10 <sup>-3</sup>	$-0,67$ $6,6\cdot 10^{-3}$					
Pigments obtained by	1:3	-0,63	$1,2 \cdot 10^{-3}$	-0,64	$1,5 \cdot 10^{-3}$			
mechanochemical	1:1	-0,45	$2,1\cdot 10^{-3}$	-0,54	$2,1\cdot 10^{-3}$			
method	3:1	-0,49	7,8·10 <sup>-3</sup>	-0,58	$13,2 \cdot 10^{-3}$			
	1:3	-0,63	$2,4\cdot 10^{-3}$	-0,62	$1,4\cdot 10^{-3}$			
Simple mixture	1:1	-0,67	$3,1\cdot 10^{-3}$	-0,60	$2,4\cdot 10^{-3}$			
	3:1	-0,45	3,6.10-3	-0,56	3,5.10-3			

It was discovered (Fig. 2, Table 2) that, after 24 h immersion in zeolite/Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> pigment extracts, a protective film is formed on the steel surface. Its morphology depends on the weight ratio of pigments components. The film formed in solutions with simple mixture of zeolite and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> is discontinuous. It cracked and peeled off from the metal surface after the water evaporated from the sample surface. Phosphorus and calcium were detected in its chemical composition. Probably, that, in addition to phosphate compounds, this film also contains iron corrosion products.

The film formed on steel in solutions with mechanochemically obtained pigments is more homogeneous and continuous. Cracking of this film is not observed. This is especially true for a pigment with a 1:3 zeolite/phosphate ratio. In this case, the calcium content is almost twice higher than after the using of a simple mixture of zeolite and phosphate. Thus, it can be assumed that, in this situation, low-soluble phosphates are more intensely deposited in the cathodic zones of the metal surface.



Fig.2. SEM images of steel after 24 h immersion in a 0.1% NaCl solution with a mixture of zeolite and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (*a*–*c*) and with pigments obtained by mechanochemical method (*d*–*f*) for the zeolite/Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> ratios: (*a*) 1:3; (*b*) 1:1; (*c*) 3:1; (*d*) 1:3; (*e*) 1:1; (*f*) 3:1. The pigments and mixture concentration was 1 g/l.

Table 2

 $\label{eq:chemical composition (wt. \%) of steel surface after 24 h immersion in a 0.1\% NaCl solution with zeolite/Ca(H_2PO_4)_2 (1 g/l)$ 

Zeolite/Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>		Element contents										
		С	0	Na	Si	Р	Ca	Mn	Fe	Cl		
pigments obtained by	1:3	-	16,4	0,8	0,6	4,6	1,2	1,0	75,4	-		
mechanochemical	1:1	-	19,2	10,3	0,5	5,6	1,7	0,7	54,7	7,3		
method	3:1	-	39,4	1,0	0,3	11,8	1,2	0,4	45,9	-		
simple mixture	1:3	-	12,6	0,5	0,8	2,8	0,6	1,0	81,5	0,2		
	1:1	4,3	20,3	0,5	0,7	5,2	0,8	0,8	67,4	I		
	3:1	-	28,7	0,8	-	13,0	0,5	-	57,0	-		

### Conclusions

A pigment based on synthetic zeolite and  $Ca(H_2PO_4)_2$  was obtained by mechanochemical method. The obtained zeolite/monocalcium phosphate pigments provided an inhibiting effect on the corrosion of 09G2S steel whose efficiency was maximum for the weight ratio of zeolite and phosphate components was 1:3. A protective film is formed on the steel surface in solutions with zeolite/phosphate pigments. Its morphology and composition depend on the weight ratio of its components. This film is mainly formed by difficultly soluble calcium and iron phosphates.

## Acknowledgments

The work was performed within the project No. 2020.02/0063 "Synthesis and properties of new complex anti-corrosion pigments for paint coatings based on aluminosilicate nanocontainers" of the National Research Foundation of Ukraine.

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