# Nanocomposites and nanomaterials

# The anti-corrosion pigments based on zeolite nanocontainer for paints coatings


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The ***aim*** of work was to study the corrosion inhibition of aluminium alloy by anticorrosive pigments obtained by the liquid phase ion exchange and mechanochemical modification of nanoporous zeolite.

***Synthesis:*** Zeolite/Zn($H_2PO_4$)$_2$ pigment was obtained by mechanochemical modification using high-energy Retsch PM 100 planetary mill. The weight ratio in the grinding mixture between dihydrogen phosphates and zeolite NaA was 1:3, 1:1, 3:1. Due to modification of the zeolite at 200 rpm for 1 h (Fig. 1), there is a redistribution of the X-ray signal intensities, which indicates a change in their structure and may be associated with the introduction of phosphate into pores of the zeolite. For zeolite modified with zinc monophosphate, at 400 rpm for 2 h, the crystal lattice is completely destroyed and the amorphous phase increased. To obtain pigments based on zeolites and phosphates, a necessary condition is the preservation of the structure of the aluminosilicate framework, in the pores of which nanosized particles of corrosion inhibitors can be intercalated. Therefore, the optimal duration of mechanochemical processing is 1–2 h at a rotational speed of the cylinder of the planetary mill of 200 rpm, since the crystalline structure of NaA zeolite is preserved under such conditions.

The modification of zeolite was carried out by liquid-phase ion-exchange method with zinc, calcium and manganese cations, using $Ca(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ salts. The salt concentration was 0.45 M. The synthesis was carried out at 70 °C under periodic mixing f

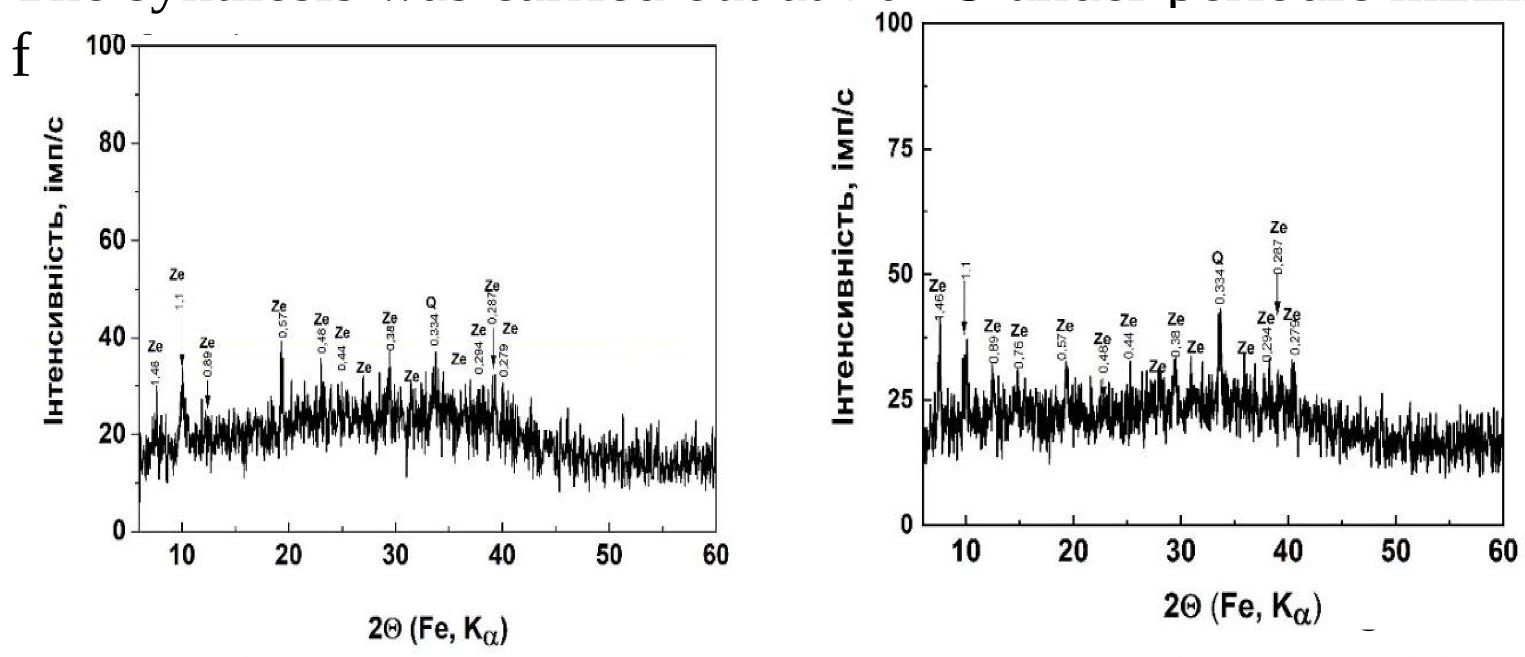



**Fig. 1** XRD of modified zeolite at 200 rpm: 1h (*a*) and 2 h (*b*)

***Results and discussion:*** The corrosion resistance of an aluminium alloy in the presence of Na-A zeolite, modified with divalent metal cations by the liquid phase ion exchange is increased in the range Ca-zeolite <Mn-zeolite <Zn-zeolite. The zeolite/Zn($H_2PO_4$)$_2$ pigments effectively reduce the corrosion current of the aluminium alloy (fig. 2).

The corrosion resistance of the alloy is significantly increased in the solution with the pigment extract compared to the non-inhibited solution. The highest anti-corrosion effect is established for zeolite/Zn($H_2PO_4$)$_2$ pigment with a concentration of 1 g/l at a 1:1 components ratio, probably due to optimal solubility of its phosphate phase (fig. 3).

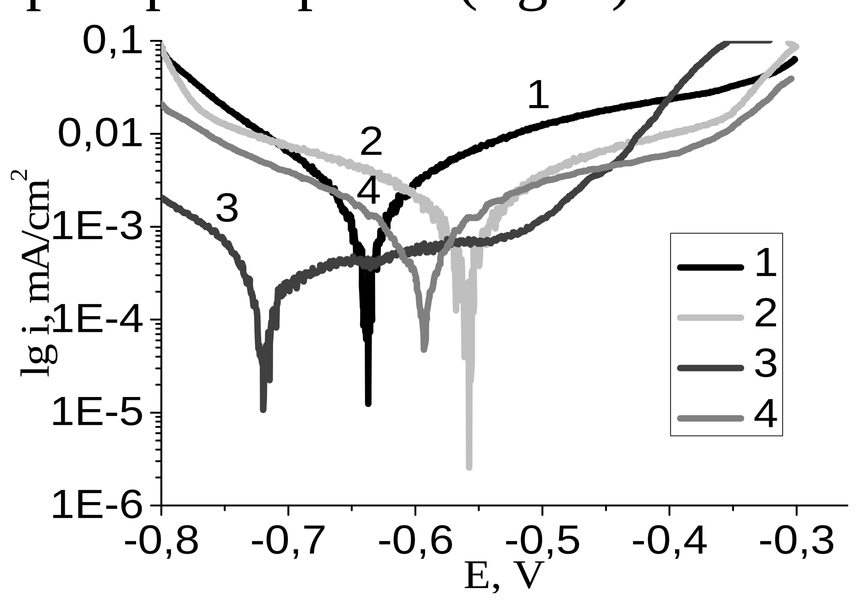



**Fig. 2** Polarization curves of D16T aluminium alloy after 24 h exposure in 0.1% NaCl solution: 1 – uninhibited, 2 – with Ca-zeolite, 3 – with Zn-zeolite, 4 – with Mn-zeolite (2 g/l)

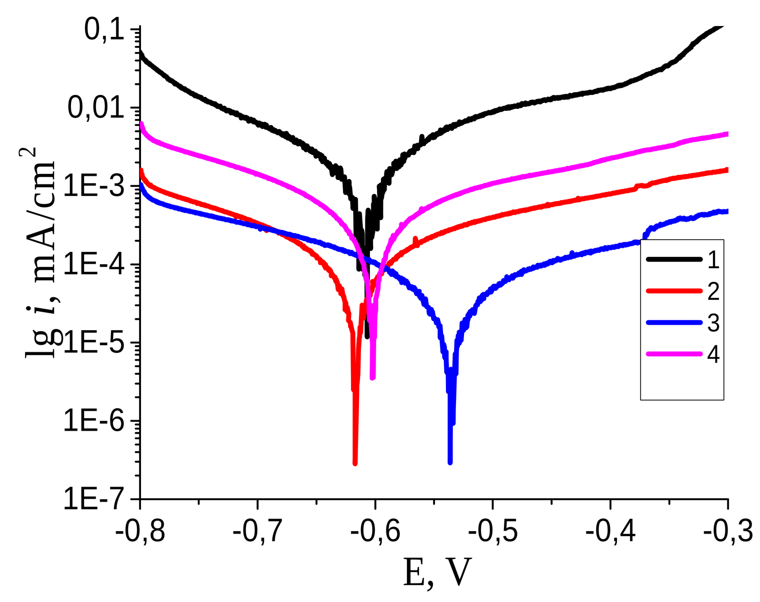



**Fig. 3** Polarization curves of D16T aluminium alloy after 96 h exposure in: 1 - 0.1% NaCl solution and with pigment (1 g/l) at zeolite/Zn($H_2PO_4$)$_2$ ratios: 2 - 3:1; 3 - 1:1; 4 - 1:3

The impedance modulus $Z_{0.1}$ at a frequency of 0.1 Hz for samples of aluminium alloy after 3 h exposure to chloride solution with 1 g/l of unmodified zeolite are the lowest (about $4.1 \cdot 10^3$ $Ohm \cdot cm^2$). This measurement indicates that the corrosion resistance of aluminium alloy in these solutions is the lowest. Addition of zeolite/Zn($H_2PO_4$)$_2$ pigments (at a concentration of 1 g/l) to the corrosion solution leads to the increase of the impedance modulus. It should be noted that the highest efficiency of corrosion inhibition by zeolite/Zn($H_2PO_4$)$_2$ pigment are at a 1:1 and 3:1 components ratio.

The use of separate inhibitory components of the mixture does not ensure high efficiency of anti-corrosion protection of the alloy.

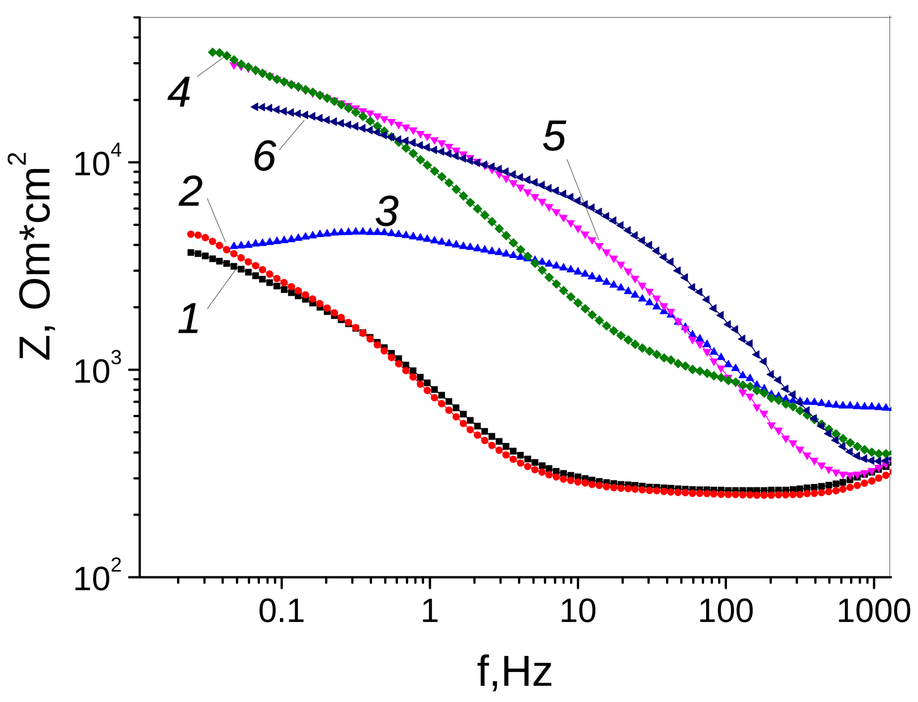
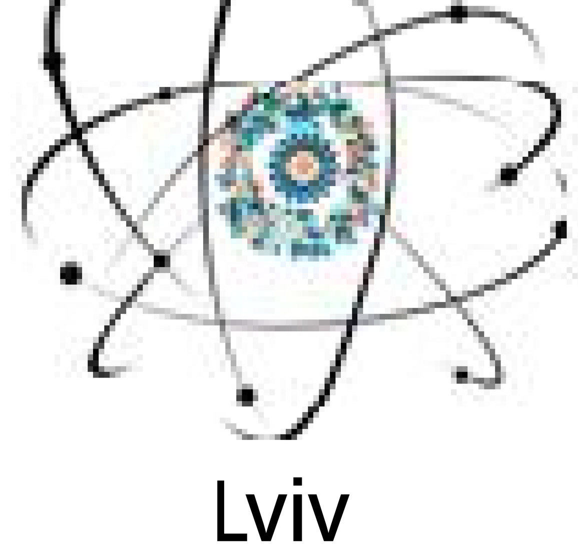



**Fig. 3** Impedance modulus dependencies for D16T alloy after 24 h exposure in: 1 – 0.1% NaCl solution and inhibited by 1 g/l of: 2 – unmodified zeolite and at different zeolite/Zn($H_2PO_4$)$_2$ ratios: 3 - 3:1; 4 - 1:1; 5 - 1:3

## Conclusions

The obtained pigments can become promising inhibitory components of paint primers for the protection of aluminium alloy structures in an industrial environment and serve as an effective alternative to the known zinc phosphate pigments.



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