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# Synthesis and characterization of the aluminium phosphates modified with ammonium, calcium and molybdenum by hydrothermal method

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Synthesis and characterization of the aluminum phosphates modified with ammonium, calcium and molybdenum were conducted. The influence of process parameters (reactive pressure and molar ratios) in the reaction mixture were studied. The contents of the individual components in the products were in the range of: 10.97–17.31 wt% Al, 2.65–13.32 wt% Ca, 0.70–3.11 wt% Mo, 4.36–8.38 wt% $NH_3$, and 35.12–50.54 wt% $P_2O_5$. The materials obtained in the experiments were characterized by various physicochemical parameters. The absorption oil number was in the range from 67 to 89 of oil/100 g of product, the surface area was within the range of 4–76 $m^2/g$, whereas the average particle size of products reached 282–370 nm. The Tafel tests revealed comparable anticorrosive properties of aluminum phosphates modified with ammonium, calcium, molybdenum in comparison with commercial phosphate.

**Keywords:** hydrothermal method, anticorrosive pigments, modified aluminum phosphates.

## INTRODUCTION

The aim of pigment mixture development is to enhance the anticorrosion efficiency of non-toxic pigments and shift their efficiency closer to the old, toxic (but very efficient) chromate and lead pigments. Such development is necessary to meet tough environmental norms that are steadily becoming stricter[1, 2, 3]. The latest EU legislation on organic coatings took effect in 2010 and was aimed at reducing volatile organic compounds in paint systems[2].

Literature reports seem to suggest that the anticorrosion properties of pigments are affected not only by their chemical composition, but also by other factors, including their particle size, oil number, specific surface area and water solubility[4, 5, 6]. Changes in the structure and chemical composition of various materials can be obtained by using different process parameters in their preparation (e.g. substrate molar ratio, the pH of a reaction mixture, reaction time, pressure, temperature) or with microwave radiation[7, 8, 9]. Microwave is an energy source which has found its applications in many scientific research areas. Microwave radiation has shown its capability for fast preparation of size controlled metallic nanostructures on different substrates[10, 11]. Microwave technique attracts more interest because it can generate heat internally inside the sample so the heat can be transferred homogeneously and rapidly. The microwave technique requires far less energy than resistive heating and is less polluting than gas or oil fired heaters and is therefore more environmentally friendly[12]. Moreover, rapid initial heating of the microwave can enhance the kinetics of the reaction due to the formation of high temperature throughout the sample[13].

The aim of the presented work was to elaborate the preparation process of aluminum phosphates modified with ammonium, calcium and molybdenum by hydrothermal method. Their steel corrosion inhibition efficiency was investigated by means of the potentiodynamic polarization technique. The influence of preparation process parameters on several physicochemical properties of the products such as chemical composition, oil absorption and specific surface area was determined. Based on the Tafel test results the corrosion potential, corrosion current density and corrosion rate for steel immersed in a phosphate extract in an aqueous NaCl solution were calculated and presented.

## EXPERIMENTAL

### Procedure

Studies on the synthesis of aluminum phosphates modified with ammonium, calcium and molybdenum were performed on the basis of the experimental planning and analysis according to a three-level $3^{(k-p)}$ fractional factorial designs with 9 experiments using the hydrothermal method. The process independent variables were: $x_1$ – the pressure (1.1 ± 1 MPa), $x_2$ – the molar ratio of $Ca^{2+}$ to $PO_4^{3-}$ in the substrates 0.2 ± 0.13 : 1 corresponding to the molar ratios of $Al^{3+}$ to $Ca^{2+}$ to $Mo^{6+}$ to $PO_4^{3-}$ in the reaction mixture (0.67 : 0.2 ± 0.13 : 0.2 ± 0.13 : 1).

The aim of the study was to obtain products with the molar ratio of $(NH_4)_3Al_2(PO_4)_3$ to $CaMoO_4$ varying in the range of 1 : (0.6 ± 0.4). Therefore, to obtain a product with the molar ratio of $(NH_4)_3Al_2(PO_4)_3$ to $CaMoO_4$ equalling 1 : 1, the reactor had to be feed with substrates in the molar ratios corresponding to those in the following reactions:

$$14Al(OH)_3 + 21(NH_4)_2HPO_4 \rightarrow 7(NH_4)_3Al_2(PO_4)_3 + 21NH_4OH + 21H_2O \quad (1)$$

$$7CaCO_3 + (NH_4)_6Mo_7O_{24} + 3H_2O \rightarrow 7CaMoO_4 + 6NH_4OH + 7CO_2 \quad (2)$$

During the experiments, it turned out that a competitive reaction involving hydroxylapatite precipitation was also proceeding:

$$3(NH_4)_2HPO_4 + 5CaCO_3 + 4NH_4OH \rightarrow Ca_5(PO_4)_3(OH) + 5(NH_4)_2CO_3 + 3H_2O \quad (3)$$

Multiple dependent variables defining the physicochemical properties of prepared products were as follows: the content of $Al^{3+}$ ($y_1$), $Ca^{2+}$ ($y_2$), $Mo^{6+}$ ($y_3$), $NH_3$ ($y_4$), $P_2O_5$ ($y_5$), oil absorption number ($y_6$), specific surface area $S_{BET}$ ($y_7$), and average particle size ($y_8$).

**Table 1.** Three-level $3^{(k-p)}$ fractional factorial design and physicochemical properties of aluminum phosphates modified with ammonium, calcium and molybdenum obtained hydrothermal conditions

| Phosphate acronym | Independent variables | | Dependent variables | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $y_3$ | $y_4$ | $y_5$ | $y_6$ | $y_7$ | $y_8$ |
| | [MPa] | | [wt%] | | | | | [g/100g] | [m$^2$/g] | [nm] |
| AACMPH1 | 0.1 | 0.07 | 17.31 | 3.50 | 1.07 | 6.41 | 43.5 | 73 | 76 | 346 |
| AACMPH2 | 1.1 | 0.07 | 17.31 | 2.98 | 0.70 | 6.51 | 44.2 | 75 | 54 | 297 |
| AACMPH3 | 2.1 | 0.07 | 15.25 | 2.65 | 0.79 | 8.38 | 50.54 | 67 | 34 | 343 |
| AACMPH4 | 0.1 | 0.2 | 14.32 | 8.47 | 1.21 | 5.65 | 40.51 | 74 | 55 | 320 |
| AACMPH5 | 1.1 | 0.2 | 13.49 | 9.45 | 1.58 | 5.78 | 40.68 | 75 | 57 | 311 |
| AACMPH6 | 2.1 | 0.2 | 13.65 | 8.95 | 2.28 | 5.74 | 41.16 | 68 | 52 | 370 |
| AACMPH7 | 0.1 | 0.33 | 10.97 | 13.32 | 3.11 | 4.36 | 35.12 | 81 | 51 | 282 |
| AACMPH8 | 1.1 | 0.33 | 11.57 | 13.11 | 3.00 | 4.98 | 40.55 | 89 | 69 | 305 |
| AACMPH9 | 2.1 | 0.33 | 11.08 | 13.09 | 2.55 | 5.71 | 42.44 | 74 | 41 | 310 |

The aim of the performed experiments according to the established plan was to determine the fractional design at 3 levels of the important factors affecting the investigated parameters and to find the right input values enabling to obtain a product with the expected properties[14]. A factorial plan and the results obtained from experiments are summarized in Table 1. Basing on the beginning studies it was take that the constant conditions process were equal to: pH of the reaction was 6 and time reaction was allowed 20 minutes. The total salt concentration amounted to 40 wt%.

**Sample preparation**

Reagent grade substrates: $(NH_4)_2HPO_4$, $CaCO_3$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, an aqueous ammonia (25 wt% of $NH_3$) and amorphous $Al(OH)_3$ were used. Aluminum hydroxide was precipitated in the reaction of aluminum nitrate with potassium hydroxide at pH = 7.5[15]. The molar ratios of $Al^{+3}$: $Ca^{2+}$: $Mo^{6+}$: $PO_4^{3-}$ in the reaction mixture amounted to 0.67 : (0.2 ±0.13) : (0.2 ±0.13) : 1. The constant process parameters were: pH of the reaction equal to 6 and the total salt concentration amounted to 40 wt%. A suspension of amorphous aluminum hydroxide and calcium carbonate was dosed into an ammonium molybdate and ammonium phosphates solution at a constant stirring velocity. The suspension of reactants with an appropriate pH was prepared in a glass reactor and the mixture was transferred into the microwave reactor and treated at a pressure of 1.1 ±1 MPa (microwave reactor type ERTEC Magnum, output 750 W at a frequency of 2.45 GHz, Ertec Poland), for 20 min. The obtained precipitate was separated from the mother liquor using a vacuous filter, followed by triple washing with distilled water (the weight ratio of the liquid to the solid phase was 3 : 1). Finally, the obtained product was dried for 3 h at 70°C.

Anticorrosive properties of the modified aluminum phosphate for cold rolled steel were investigated by means of the potentiodynamic polarization technique. For comparison purposes, two commercial anticorrosive pigments, i.e. zinc phosphate and zinc aluminum phosphate (FC-M2, FAC) were tested.

**Sample characterization**

The content of aluminum, calcium and molybdenum in the products was determined by ICP-AES analysis (Optima 5300 DV, Perkin Elmer). The phosphates and ammonium contents were determined using a spectrophotometric method[15] and ion selective electrode Orion 11–35 type, respectively[16]. The phase composition of the products was studied with X-ray diffraction analysis (Cu$K_{\acute{a}}$ radiation, X'Pert PRO Philips diffractometer). The oil absorption (grams of oil required to form a homogeneous paste with 100 g of the tested dry pigment) was determined according to PN-EN ISO 787-5 standard[17]. The measurements of Brunauer-Emmett-Teller surface area ($S_{BET}$) of the materials were performed using Micrometrics Quadrasorb SI Quantachrome Instrument. $N_2$ adsorption/desorption measurements were carried out at liquid $N_2$ temperature. The average particle size of the materials was determined using a laser scanning microscope (VK-9700, Keyence, USA). The phosphate morphology was examined with a scanning electron microscope SU-70 (Hitachi, Japan). The chemical composition of the phosphates was determined using a scanning electron microscope with a cold field emission (HITACHI SU8020, resolving power 1.3 nm), coupled with the energy dispersive X-ray analyzer (EDX – Thermo Scientific).

Tafel experiments in the range from –250 to 500 mV in relation to OCP (scan rate 0.25 mV $s^{-1}$) for an uncoated steel substrate (SEA 1008/1010, Q-Panels, Q-Lab Europe, England) were performed using DC105 software and FAS2 femtostat (Gamry, USA). As a result, corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and corrosion rate ($P$) were determined using Echem Analyst software (Gamry). Steel polarization was carried out using electrolytes prepared by shaking a phosphate filler (2.5 g) with 100 g of 3.5 wt% NaCl aqueous solution for 2 h (i.e. twice for 1 h with a 22 h interval). Then, the suspension was centrifuged (4000 rpm, 10 min) and an aqueous extract was carefully decanted. The Tafel tests were made after 20 h of a glass cell filling with an electrolyte (aqueous NaCl solution or phosphate extract). The corrosion inhibition efficiency (η, %) of phosphate extracts was calculated according to the following equation:

$$\eta = \left[\frac{i_0 - i}{i_0}\right] \times 100 \qquad (1)$$

where $i_0$ and $i$ are corrosion current densities registered for steel substrate immersed in a 3.5 wt% NaCl aqueous solution and the aqueous extract of phosphate filler, respectively.

## RESULTS AND DISCUSSION

Figure 1 and Table 2 shows the phase composition of the precipitated products, which was determined

**Table 2.** The phase composition and molar ratio of the components in obtained products

| Phosphate acronym | Independent variables | | Phase composition (peak intensity) | | | Molar ratio |
|---|---|---|---|---|---|---|
| | $x_1$ [MPa] | $x_2$ | $(NH_4)_3Al_2(PO_4)_3$ | $Ca_5(PO_4)_3(OH)$ | $CaMoO_4$ | $Al^{3+}$:$Ca^{2+}$:$Mo^{6+}$:$NH_4^+$:$PO_4^{3-}$ |
| AACMPH1 | 0.1 | 0.07 | *** | ** | – | 1.0 : 0.1 : 0.02 : 0.62 : 1 |
| AACMPH2 | 1.1 | | *** | ** | – | 1.0 : 0.1 : 0.01 : 0.62 : 1 |
| AACMPH3 | 2.1 | | *** | ** | – | 0.8 : 0.1 : 0.01 : 0.69 : 1 |
| AACMPH4 | 0.1 | 0.2 | ** | ** | ** | 0.9 : 0.4 : 0.02 : 0.58 : 1 |
| AACMPH5 | 1.1 | | ** | ** | ** | 0.9 : 0.4 : 0.03 : 0.59 : 1 |
| AACMPH6 | 2.1 | | ** | ** | ** | 0.9 : 0.4 : 0.04 : 0.58 : 1 |
| AACMPH7 | 0.1 | 0.33 | * | ** | *** | 0.8 : 0.7 : 0.07 : 0.52 : 1 |
| AACMPH8 | 1.1 | | * | ** | *** | 0.8 : 0.6 : 0.05 : 0.51 : 1 |
| AACMPH9 | 2.1 | | * | *** | *** | 0.7 : 0.5 : 0.04 : 0.56 : 1 |

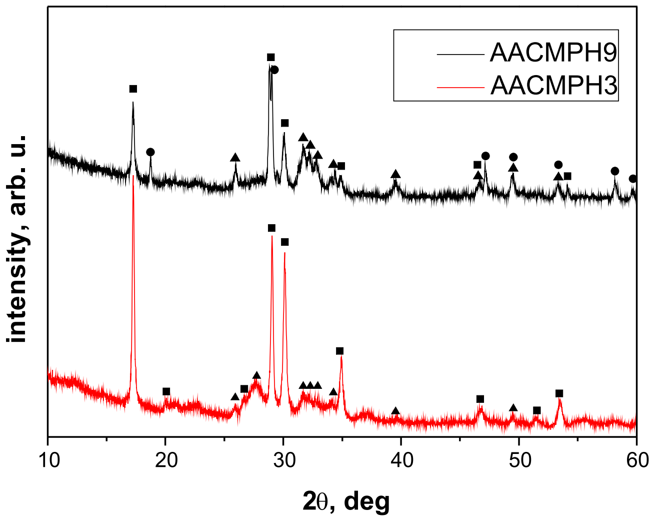


**Figure 1.** X-ray diffraction patterns of products obtained (AACMPH3 and AACMPH9) [■] $(NH_4)_3Al_2(PO_4)_3$; [●] $CaMoO_4$; [▲] $Ca_5(PO_4)_3(OH)$

using XRD analysis. $(NH_4)_3Al_2(PO_4)_3$, $CaMoO_4$ and $Ca_5(PO_4)_3(OH)$, crystalline compounds, were identified. Their ratio varied depending on the composition of substrate mixture. For the lowest molar ratio of $Al^{3+}$: $Ca^{2+}$ in the initial mixture equalling 2 ($Al^{3+}$: $Ca^{2+}$ 0.67 : 0.33), the content of $CaMoO_4$ in the products was the highest. However, the higher was the molar ratio of reagents containing aluminum and calcium, the higher was the content of $(NH_4)_3Al_2(PO_4)_3$ in the precipitated solid phases.

The chemical composition of the obtained materials mainly depended on the substrate molar ration which determined the phase composition. Products with a higher molar ratio between $(NH_4)_3Al_2(PO_4)_3$ and $CaMoO_4$ contained more aluminum and ammonia and less calcium and molybdenum. Therefore, products in each group had similar chemical and phase compositions: I – AACMPH1-3, II – AACMPH4-6, III – AACMPH7-9. Similarly, products from different groups had different chemical and phase compositions (Tables 1 and 2). The precipitated products were in the range of: 10.97–17.31 wt% Al, 2.65–13.32 wt% Ca, 0.70–3.11 wt% Mo, 4.36–8.38 wt% $NH_3$, and 35.12–50.54 wt% $P_2O_5$ (Table 1).

A statistical analysis, focused on determining process parameters that had a significant influence on the physicochemical properties of the obtained phosphates, was conducted to assess the effects of changes in input values $y_{1–8}$ for the extremum input values $x_{1,2}$. Pareto charts were drawn to illustrate the trends (Fig. 2). To confirm the assessment significance of obtained effects, Anova analysis was performed (Table 3).

The molar ratio of $Ca^{2+}$ to $PO_4^{3-}$ in substrates ($x_2$) was found to have a statistically significant effect on aluminum content ($y_1$) in the products. Bearing in mind that (x2(L), effect–5.42) has a negative number (Table 3), it was fair to think that a lower values of $x_2$ would result in the increase of the dependent variable $y_1$ .

Therefore, aluminum phosphates modified with ammonium, calcium and molybdenum with a higher content of aluminum (the average content of 16.6 wt% Al) were to be precipitated from the reaction mixture with the $Al^{3+}$ : $Ca^{2+}$ : $Mo^{6+}$ : $PO_4^{3-}$ molar ratio of 0.67 : 0.07 : 0.07 : 1.

The molar ratio of reagents ($x_2$) was found to have the highest statistic effect on calcium content ($y_2$) in the products. The positive effect ($x_2$(L), effect 10.13) of this influence seems to indicate the increase of $y_2$ values, starting from approximately 3 wt% Ca to about 13 wt% Ca along with the increase of $x_2$ from 0.07 : 1 to 0.33 : 1 (Table 3). The dependent variable $y_{3,}$ denoting molybdenum content in the obtained phosphates, also depended on the molar ratio of $Ca^{2+}$ : $PO_4^{3-}$ in the reaction mixture. The statistical analysis demonstrated the positive sign of the effect ($x_2$(L), effect 2.03) which translated into the increase of molybdenum content in the products (from approximately 0.8 wt% to about 3 wt%) along with the increase of the independent variable (Table 3).

The content of ammonium groups (the dependent variable $y_4$) in the obtained products also depended on the $Ca^{2+}$ : $PO_4^{3-}$ ratio in the reaction mixture ($x_2$(L), effect –2.08). It was found that the less calcium (and at the same time molybdenum) was introduced into the reaction mixture, the higher was the content of nitrogen in the products. It increased from approximately 5 wt% $NH_3$ to about 7 wt% $NH_3$.

It was demonstrated that another dependent variable $y_6$, i.e. the content of phosphates in the products was affected only by the molar ratio of the substrates. Following the analysis of effect assessment ($x_2$(L) –6.71), the highest content of phosphates in the obtained products was observed for the $Ca^{2+}$ : $PO_4^{3-}$ molar ratio of 0.07 : 1 in the reaction mixture.

It was statistically demonstrated that the above discussed input variables correlated with the chemical composition of the products were not affected by the pressure of the process (0.1–2.1 MPa).

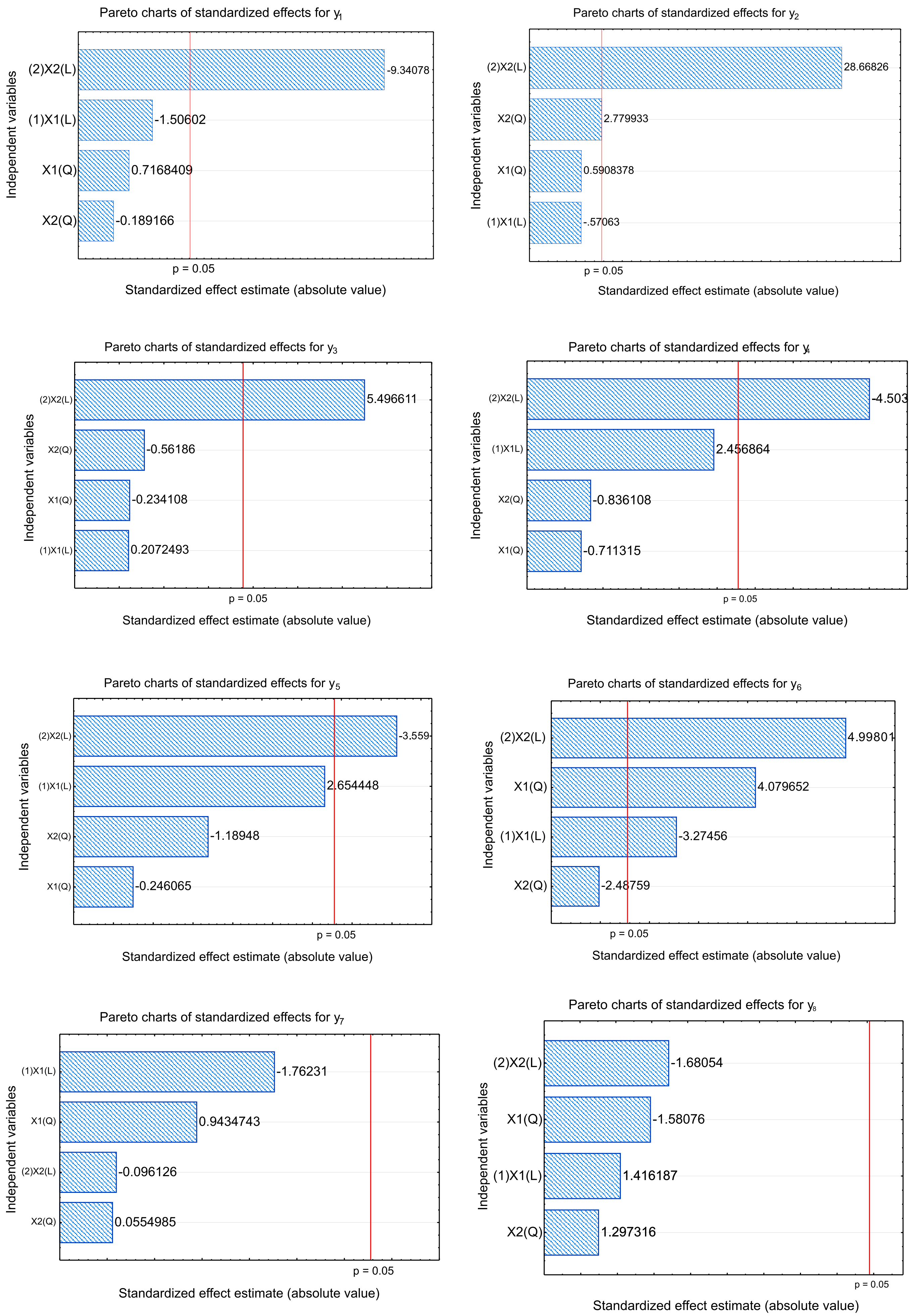


**Figure 2.** Pareto charts of standardized $y_{1–8}$

**Table 3.** ANOVA table analysis for dependent variables ($y_1$–$y_8$)

| Independent variables | Effect | Std. Error | t[4] | p | 95% Confidence Interval for Difference | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| | | | $y_1$ | | | |
| Mean/constant | 13.88333 | 0.236741 | 58.64356 | 0.000001 | 13.22603 | 14.54063 |
| (1)X1(L) | –0.87333 | 0.579895 | –1.50602 | 0.206526 | –2.48338 | 0.73671 |
| X1(Q) | 0.36000 | 0.502203 | 0.71684 | 0.513101 | –1.03434 | 1.75434 |
| **(2)X2(L)** | **–5.41667** | **0.579895** | **–9.34078** | **0.000731** | **–7.02671** | **–3.80662** |
| X2(Q) | –0.09500 | 0.502203 | –0.18917 | 0.859173 | –1.48934 | 1.29934 |
| | | | $y_2$ | | | |
| Mean/constant | 8.39111 | 0.144279 | 58.15881 | 0.000001 | 7.99053 | 8.79169 |
| (1)X1(L) | –0.20167 | 0.353411 | –0.57063 | 0.598778 | –1.18289 | 0.77956 |
| X1(Q) | 0.18083 | 0.306063 | 0.59084 | 0.586398 | –0.66893 | 1.03060 |
| **(2)X2 (L)** | **10.13167** | **0.353411** | **28.66826** | **0.000009** | **9.15044** | **11.11289** |
| **X2(Q)** | **0.85083** | **0.306063** | **2.77993** | **0.049822** | **0.00107** | **1.70060** |
| | | | $y_3$ | | | |
| Mean/constant | 1.810000 | 0.151021 | 11.98507 | 0,000278 | 1.39070 | 2.229302 |
| (1)X1(L) | 0.076667 | 0.369925 | 0.20725 | 0,845938 | –0.95041 | 1.103743 |
| X1(Q) | –0.075000 | 0.320364 | –0.23411 | 0,826395 | –0.96447 | 0.814474 |
| **(2)X2(L)** | **2.033333** | **0.369925** | **5.49661** | **0,005340** | **1.00626** | **3.060410** |
| X2(Q) | –0.180000 | 0.320364 | –0.56186 | 0.604202 | –1.06947 | 0709474 |
| | | | $y_4$ | | | |
| Mean/constant | 5.94667 | 0.188876 | 31.48453 | 0.000006 | 5.42226 | 6.471070 |
| (1)X1(L) | 1.13667 | 0.462649 | 2.45686 | 0.069927 | –0.14785 | 2.421187 |
| X1(Q) | –0.28500 | 0.400666 | -0.71132 | 0.516171 | –1.39743 | 0.827427 |
| **(2)X2(L)** | **–2.08333** | **0.462649** | **-4.50305** | **0.010797** | **–3.36785** | **–0.798813** |
| X2(Q) | –0.33500 | 0.400666 | -0.83611 | 0.450132 | -1.44743 | 0.777427 |
| | | | $y_5$ | | | |
| Mean/constant | 42.07778 | 0.769502 | 54.68186 | 0.000001 | 39.9413 | 44.21426 |
| (1)X1(L) | 5.00333 | 1.884886 | 2.65445 | 0.056718 | –0.2299 | 10.23662 |
| X1(Q) | –0.40167 | 1.632359 | –0.24607 | 0.817743 | –4.9338 | 4.13049 |
| **(2)X2(L)** | **–6.71000** | **1.884886** | **–3.55990** | **0.023588** | **–11.9433** | **–1.47672** |
| X2(Q) | –1.94167 | 1.632359 | –1.18948 | 0.300029 | –6.4738 | 2.59049 |
| | | | $y_6$ | | | |
| Mean/constant | 75.11111 | 0.789593 | 95.12639 | 0.000000 | 72.9189 | 77.30337 |
| **(1)X1(L)** | **–6.33333** | **1.934099** | **–3.27456** | **0.030657** | **–11.7033** | **–0.96341** |
| **X1(Q)** | **6.83333** | **1.674979** | **4.07965** | **0.015103** | **2.1828** | **11.48382** |
| **(2)X2(L)** | **9.66667** | **1.934099** | **4.99802** | **0.007501** | **4.2967** | **15.03659** |
| X2(Q) | –4.16667 | 1.674979 | –2.48759 | 0.067659 | –8.8172 | 0.48382 |
| | | | $y_7$ | | | |
| Mean/constant | 54.3333 | 4.24700 | 12.79333 | 0.000215 | 42.5418 | 66.12490 |
| (1)X1(L) | –18.3333 | 10.40299 | –1.76231 | 0.152804 | –47.2167 | 10.55000 |
| X1(Q) | 8.5000 | 9.00925 | 0.94347 | 0.398860 | –16.5137 | 33.51370 |
| (2)X2(L) | –1.0000 | 10.40299 | –0.09613 | 0.928044 | –29.8833 | 27.88333 |
| X2(Q) | 0.5000 | 9.00925 | 0.05550 | 0.958403 | –24.5137 | 25.51370 |
| | | | $y_8$ | | | |
| Mean/constant | 320.4444 | 7.20682 | 44.46405 | 0.000002 | 300.4351 | 340.4538 |
| (1)X1(L) | 25.0000 | 17.65303 | 1.41619 | 0.229663 | –24.0127 | 74.0127 |
| X1(Q) | –24.1667 | 15.28798 | –1.58076 | 0.189087 | –66.6129 | 18.2796 |
| (2)X2(L) | –29.6667 | 17.65303 | –1.68054 | 0.168148 | –78.6793 | 19.3460 |
| X2(Q) | 19.8333 | 15.28798 | 1.29732 | 0.264287 | –22.6129 | 62.2796 |

The statistical analysis of the effect of independent variables ($x_1$, $x_2$) on the dependent variables characterizing the morphology of materials demonstrated that the substrate molar ratio in the reaction mixture ($x_2$(L) 9.67) and the pressure of the process ($x_1$(L) –6.33) had a statistically significant influence on their oil number ($y_6$). The lower the pressure and the higher the $Ca^{2+}$:$PO_4^{3-}$ molar ratio, the higher oil number tended to be, characterizing the sorption properties of the products. Both of the input variables had no effect on the specific surface area and on the average particle size of the precipitated phosphates. Their specific surface area ($y_7$) and particle size ($y_8$) were in the range of 34–76 $m^2/g$ and 280–370 nm, respectively.

The spatial graphs in Figure 2 show the effect of pressure and $Ca^{2+}$: $PO_4^{3-}$ ratio in the reaction mixture on the dependent variables $y_{1-8}$. The depicted areas can help to assess the influence of the above process parameters on the properties of precipitated phosphates. Based on that, a conclusion was drawn that only the substrate molar ratio affected the content of aluminum, calcium and molybdenum in the products, which is consistent with the results of the statistical analysis. The specific surface area was found to be slightly affected by the pressure of the process, which in the statistical assessment of the effects was described to have a negligible effect.

The shape of the surface presented in Figure 3, depicting the effect of variables $x_1$ and $x_2$ on the oil number of the products, suggest the influence of both parameters with a maximum observed for the average pressure. The finding is consistent with the statistical analysis of ($x_2$(L) 9.67; $x_1$(L) –6.33; $x_1$(Q) 6.83) effects. However, the interpretation of the shape in terms of the effect of the independent variables on the content of nitrogen

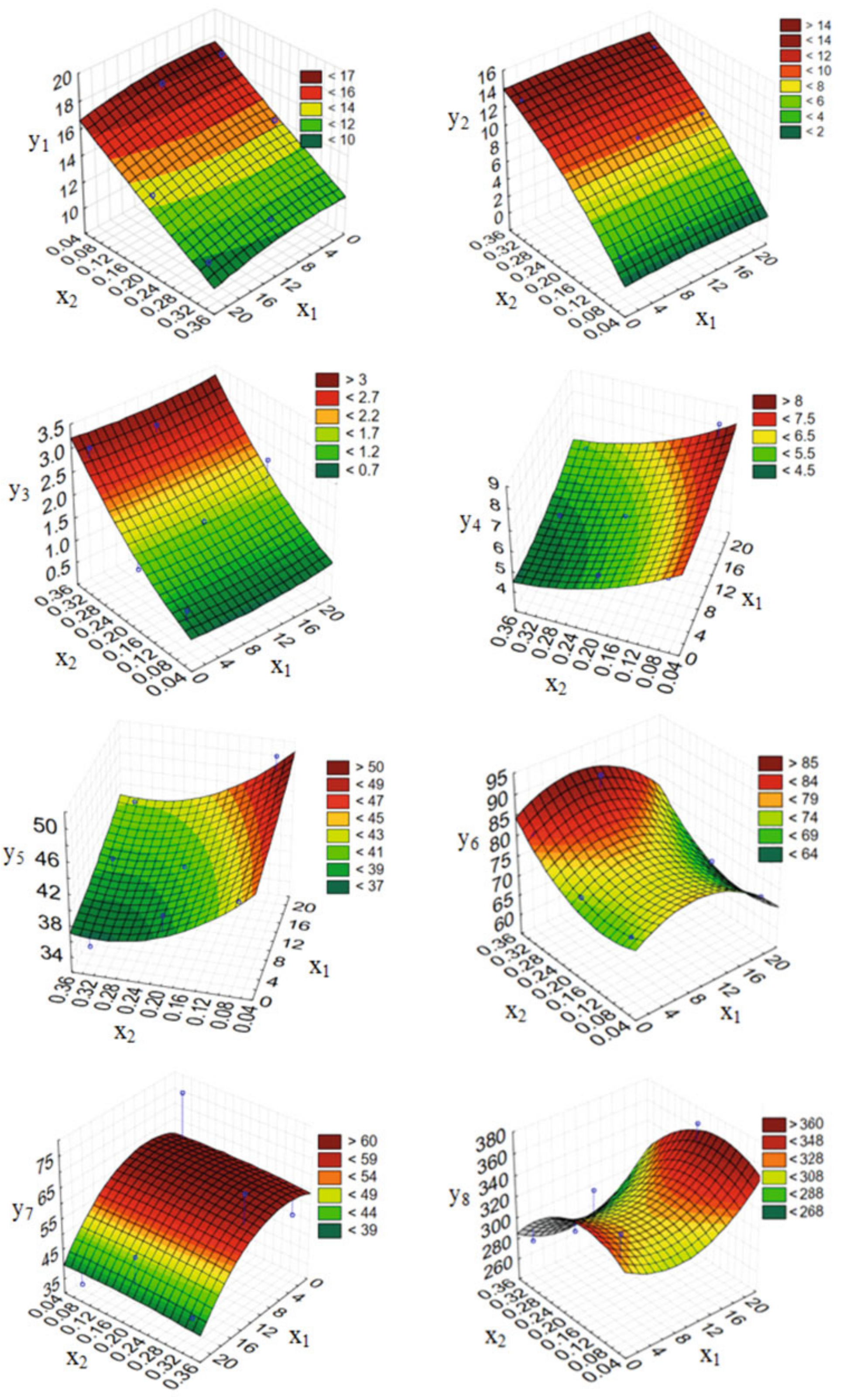

**Figure 3.** Response surface for dependent variables $x_{1-2}$ to independent variables $y_{1-8}$

and phosphates and the particle size ($y_4$, $y_5$, and $y_8$) in the products, is anything but an easy task.

The molar ratio of the substrates had a significant effect on the first two input variables. However, the shape of the surface seems to suggest the effect of the pressure of the process. The effect of variables $x_1$ and $x_2$ on the particle size of the precipitated phosphates was thought to be statistically insignificant. The surface analysis suggests that products with the biggest particle size can be obtained at the $Ca^{2+}$: $PO_4^{3}$ molar ratio of 0.2 : 1 and maximum pressure values.

Figure 4 presents a comparison of SEM images for the products precipitated in the reaction mixture with the $Al^{3+}$: $Ca^{2+}$: $Mo^{6+}$: $PO_4^{3-}$ molar ratios of (a) 0.67 : 0.33 : 0.33 : 1 (a); 0.67 : 0.2 : 0.2 : 1 (b), and 0.67 : 0.07 : 0.07 : 1 and (c) at the pressure of 2.1 MPa. The shape of particles was observed to be dependent on the molar ratio of the reagents. With the decreasing content of $Ca^{2+}$ and $Mo^{6+}$ ions in the substrates, the product particle size was bigger. The observed associations correlated with the content of the $(NH_4)_3Al_2(PO_4)_3$ crystalline phase, whose share was bigger at the lower $Al^{3+}$ : $Ca^{2+}$: $Mo^{6+}$: $PO_4^{3-}$ reagent molar ratio of 0.67 : 0.07 : 0.07 : 1. The particles of products with the highest content of the crystalline phase had the biggest size, although the statistical assessment did not show any effect of the reagent molar ratio on the property.

The relationship between the chemical composition of the prepared aluminum phosphates modified with ammonium, calcium and molybdenum and their corrosion inhibition efficiency was investigated using the presented Tafel test results.

Table 4 presents the results of corrosion inhibition efficiency tests for different extracts. The results were compared with those of FC-M2 zinc phosphate and FAC

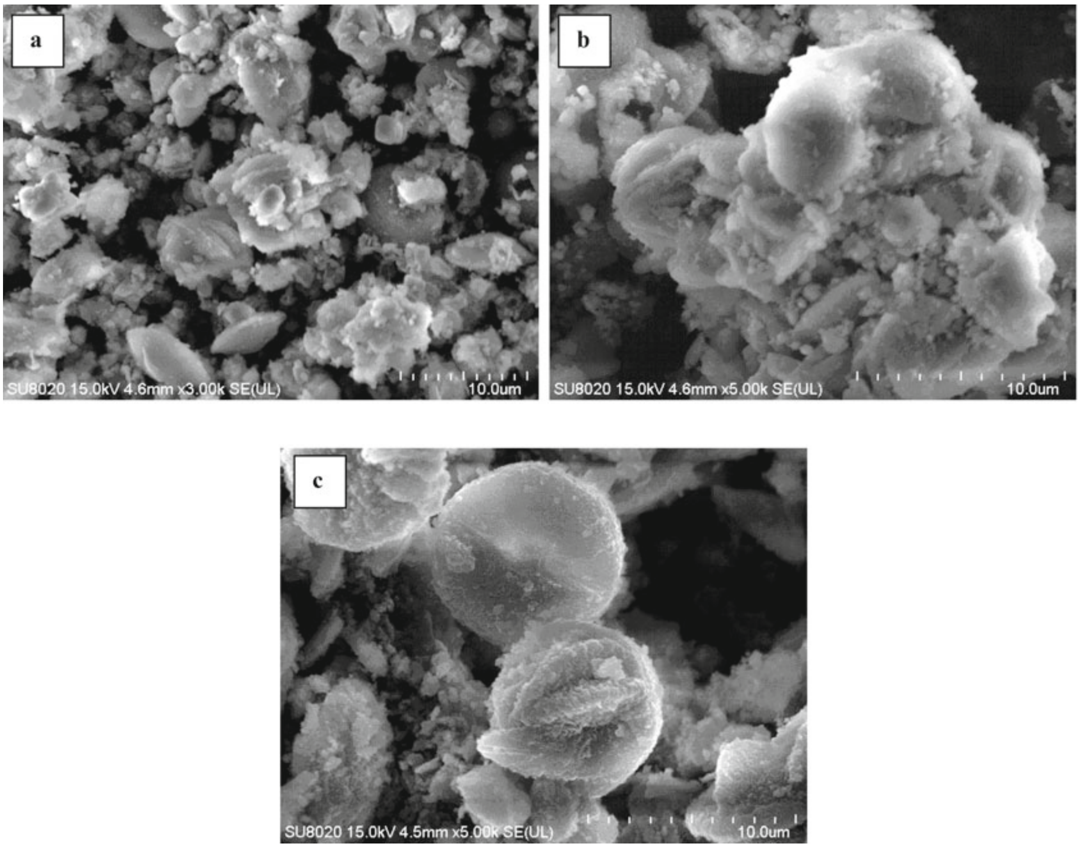


**Figure 4.** SEM images of the aluminum phosphates modified ammonium, calcium and molybdenium precipitated from reaction mixture with a molar ratio $Al^{3+}$ : $Ca^{2+}$ : $Mo^{6+}$ : $PO_4^{3-}$ equal: (a) 0.67 : 0.33 : 0.33 : 1; (b) 0.67 : 0.2 : 0.2 : 1 (b) and (c) 0.67 : 0.07 : 0.07 : 1 at the pressure of 2.1 MPa

**Table 4.** Potentiodynamic polarization test result for steel immersed in extract of phosphate pigments in 3.5 wt% NaCl aqueous solution

| Phosphate acronym | $I_{corr}$ [μA/cm$^2$] | $E_{corr}$ [mV vs. SCE] | P [mm/year] | η [%] |
|---|---|---|---|---|
| – | 2.17 | –799 | 0.025 | – |
| **FAC** | **1.1** | **–725** | **0.013** | **49** |
| **FC-M2** | **1.2** | **–796** | **0.014** | **45** |
| AACMPH1 | 2.71 | –775 | 0.0316 | –25 |
| **AACMPH2** | **1.13** | **–779** | **0.0132** | **48** |
| **AACMPH3** | **1.44** | **–767** | **0.0168** | **34** |
| AACMPH4 | 2.81 | –767 | 0.0327 | –29 |
| AACMPH5 | 1.91 | –771 | 0.0222 | 12 |
| AACMPH6 | 2.26 | –776 | 0.0263 | –4 |
| AACMPH7 | 2.16 | –779 | 0.0251 | 0.5 |
| AACMPH8 | 2.14 | –772 | 0.0249 | 1.4 |
| AACMPH9 | 1.99 | –776 | 0.0232 | 8 |

aluminum-zinc phosphate (manufactured by Złoty Stok Antykorozja Sp. z o.o. in Złoty Stok, Poland).

Following the analysis of results, the corrosion of steel was concluded to proceed the slowest with AACMPH2 and 3 materials out of all the tested extracts of modified aluminum phosphates, precipitated in a microwave reactor. The rates of corrosion for AACMPH2 and 3 were 0.0132 mm/year and 0.0168 mm/year, respectively. While comparing the obtained results with those of steel investigated in a NaCl aqueous solution, the corrosion inhibition efficiency for phosphates obtained in the experiments was 48% and 34%, respectively. The effectiveness was close to that of commercial anti-corrosive pigments (FAC and FC-M2). The lowest corrosion inhibition efficiency was determined for phosphates used in the experiments involving AACMPH1 and 4, which amounted to –25% and –29%, respectively. Corrosion was observed to proceed with the slowest rate in the phosphate extracts with the lowest Ca to Mo molar ratio and with a higher total amount of aluminum and ammonium moles per one mole of phosphates.

Sediments precipitated in Tafel tests (Table 5) were examined using XRD and SEM-EDX analysis. Unfortunately, the identification of the crystalline phases in obtained powders was impossible due to their amorphous nature. The powders had different contents of aluminum, calcium, iron and phosphates. Molybdenum content was not determined. No correlation was found between the chemical properties of the extracted phosphates, the corrosion inhibition efficiency examined in potentiodynamic tests and the chemical composition of corrosion products.

**Table 5.** EDX analysis of sediments precipitated during the electrochemical studies

| Phosphate acronym | Al | Ca | Mo | Fe | P | Molar ratio of Al : Ca : Mo : Fe : P |
|---|---|---|---|---|---|---|
| | Content [wt%] | | | | | |
| AACMPH1 | 2.49 | 0.44 | 0 | 15.41 | 3.18 | 0.90 : 0.11 : 0 : 2.69 : 1 |
| AACMPH2 | 1.77 | 0.03 | 0 | 2.43 | 0.10 | 20.30 : 0.23 : 0 : 13.47 : 1 |
| AACMPH3 | 0.58 | 0.29 | 0 | 22.98 | 5.39 | 0.12 : 0.04 : 0 : 2.36 : 1 |
| AACMPH4 | 14.32 | 2.90 | 0 | 31.08 | 2.07 | 7.94 : 1.08 : 0 : 8.33 : 1 |
| AACMPH5 | 1.99 | 0.34 | 0 | 4.89 | 1.55 | 1.47 : 0.17 : 0 : 1.75 : 1 |
| AACMPH6 | 4.71 | 1.02 | 0 | 31.30 | 2.29 | 2.36 : 0.34 : 0 : 7.58 : 1 |
| AACMPH7 | 11.29 | 1.67 | 0 | 53.27 | 0.97 | 13.35 : 1.33 : 0 : 30.45 : 1 |
| AACMPH8 | 4.38 | 0.91 | 0 | 7.78 | 1.98 | 2.54 : 0.36 : 0 : 2.18 : 1 |
| AACMPH9 | 2.36 | 0.63 | 0 | 14.46 | 2.53 | 1.07 : 0.19 : 0 : 3.17 : 1 |

## CONCLUSIONS

Crystalline materials with varied content of nitrogen, aluminum, molybdenum, calcium, phosphorus and crystalline phases depending on process parameters were obtained using the hydrothermal method.

It was statistically demonstrated that the content of Al, Ca, Mo, N and P in the products was dependent on the variable $x_2$, i.e. on the $Al^{3+} : Ca^{2+} : Mo^{6+} : PO_4^{3-}$ reagent molar ratio. The input variable $x_1$ (pressure) had no statistically significant effect on the dependent variables $y_{1–5}$. The input variables did not have any statistically significant effect on either $S_{BET}$ specific surface area or the particle size of the obtained products. The pressure and the reagent molar ratio were shown to have a significant effect on oil number.

The highest corrosion inhibition efficiency for the phosphates discussed above was 48% and 34%, respectively. The efficiency was close to that of commercial anti-corrosive pigments (FAC and FC-M2) which were used for comparison purposes.

The statistical assessment of planned examinations enables a selection of process parameters conducive to obtaining aluminum phosphates modified with ammonia, calcium and molybdenum with preset physicochemical properties.

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