Studies on obtaining of aluminium ammonium calcium phosphates

Kinga Łuczka [a,*], Barbara Grzmil [a], Joanna Sreńscek-Nazzal [a], Krzysztof Kowalczyk [b]

[a] Institute of Chemical and Environment Engineering, ul. Pułaskiego 10, 70 322 Szczecin, Poland
[b] Polymer Institute, West Pomeranian University of Technology, ul. Pułaskiego 10, 70 322 Szczecin, Poland

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ABSTRACT

Aluminium ammonium calcium phosphates were prepared with the use of $AlCl_3$, $CaCO_3$, H_3PO_4. The influence of the process parameters (pH 5 ± 3, the molar ratios of $Ca^{2+}:Al^{+3}:PO_4^{-3}$ in the substrates, respectively 0.31:0.62:1; 0.5:0.5:1; 0.72:0.36:1, temperature $40 \pm 20\,°C$) on the phase composition and the product properties was determined. The process parameters that enable to obtain the material with expected physicochemical properties were determined based on the statistical evaluation of the experiments (fractional factorial design at three levels $3^{(k-p)27}$). The phase composition of the obtained samples was studied with the use of XRD analysis. The specific surface area was calculated with the use of S_{BET} method and the particle size was determined by the laser scanning microscopy. The materials with the molar ratio of Al^{3+}/NH_4^+ and Al^{3+}/Ca^{2+} in the range of 0.70–27.93 and 0.47–24.48, respectively, with an absorption oil number of 95–157 g/100 g paraffin oil, the S_{BET} within 25–118 m^2/g, the pore volume within 0.14–0.74 cm^3/g and the particle size in the range of 168–285 nm were obtained.

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1. Introduction

Atmospheric corrosion causes the largest economic losses among all known types of corrosion. It has been evaluated that the costs of protection against corrosion amount about 70% of the expenses spent for all kinds of anti-corrosive protection [1]. A significant group of substances exhibiting the inhibitory action in the paint coating constitute the active passivated pigments which action relies mainly on the inhibition of anodic process of metal dissolution [2]. Corrosion inhibitors are generally used in small concentrations, and they should not only reduce corrosion, but also be compatible with the environment [3].

Until recently, 70% of manufactured priming paints contained in their composition two basic active pigments: lead tetroxide (minium) and chromium compounds, mainly zinc potassium chromate, commonly named zinc chromate. These compounds were withdrawn from the market due to the health and environmental risk. An extensive research is ongoing for new, effective, environmentally friendly pigments that inhibit the corrosion processes. A significant group of environmentally friendly anti-corrosive pigments constitute phosphate compounds which can be divided, among others, into the pigments of the first, second and third generation [4–7]. The anticorrosive effectiveness of phosphate pigments was tested in various types of paints [4–11]. Zubielewicz and Gnot [12] concluded that

calcium zinc phosphate and zinc ferrite exhibit the best performance due to the steel surface passivation. It has been demonstrated [6] that the second generation phosphates (aluminium zinc phosphate, iron (II) zinc phosphate, zinc phosphomolybdate), used in the acidic medium, are characterized by the improved corrosion inhibiting properties which are similar to zinc chromate. The anti-corrosive properties of Al ortho-, poly- and metaphosphates, Al Zn and Al Sr polyphosphates, or Al Ca, Ca Zn and Al silicapolyphosphates were tested in acrylic and styrene-acrylic coatings [13,14].

The protective action of active anti-corrosive pigments on metal alloys and their surfaces was also described in the literature [15]. Non-toxic materials prepared from the mixture of β-tri-calcium magnesium phosphate and calcium phosphate dihydrate were used as the anti-corrosive pigments.

Substances used in paints as the pigments must be finely dispersed in a binder. Until recently, raw materials used for the production of paints and lacquers were crushed in the ball mills with the addition of oils or other natural binders. The diameter of obtained pigment particles is usually within the range of 1–5 μm.

A corrosion inhibitor can mitigate corrosion in two ways. It can change the corrosive environment into a noncorrosive or less corrosive through its interaction with the corrosive species. In other cases, the corrosion inhibitor interacts with the metal surface and ensures the protection of metal against corrosion. Based on the mode of interactions, there are two classes of inhibitors: environment modifiers and adsorption inhibitors [3].

The majority of coloured and covering pigments as well as the speciality pigments are prepared synthetically in the processes of

* Corresponding author. Tel.: +48 91 4494730; fax: +48 91 4494686.
E-mail address: kluczka@zut.edu.pl (K. Łuczka).

Table 1
Characteristics of the prepared materials.

No.	Independent variables			The molar ratio of $Al^{3+}:Ca^{2+}:NH_4^+$: PO_4^{3-} in products	Dependent variables						Phase composition of products
	x_1	x_2	x_3		y_1	y_2	y_3	y_4	y_5	y_6	
1.	2	0.5	20	0.80:0.05:0.04:1	19.65	16.19	119	58	0.56	236	Amorphous phase
2.	2	0.5	40	0.78:0.03:0.08:1	9.83	24.48	136	49	0.48	179	
3.	2	0.5	60	0.73:0.10:0.14:1	5.29	7.20	112	49	0.51	168	
4.	2	1	20	0.68:0.12:0.11:1	6.42	5.60	111	39	0.25	192	
5.	2	1	40	0.68:0.14:0.08:1	8.04	4.93	157	25	0.16	268	
6.	2	1	60	0.72:0.12:0.04:1	16.40	6.18	122	37	0.14	174	
7.	2	2	20	0.38:0.78:0.11:1	3.47	0.48	115	59	0.18	230	Amorphous phase+trace
8.	2	2	40	0.63:0.32:0.02:1	27.93	1.98	106	48	0.21	227	amounts crystalline phase
9.	2	2	60	0.58:0.57:0.08:1	7.42	1.03	107	50	0.14	257	($CaHPO_4 \cdot 2H_2O$, $CaCO_3$)
10.	5	0.5	20	0.65:0.37:0.43:1	1.51	1.77	107	78	0.50	250	Amorphous phase
11.	5	0.5	40	0.63:0.33:0.78:1	0.81	1.88	128	70	0.45	229	
12.	5	0.5	60	0.64:0.34:0.50:1	1.28	1.88	131	82	0.51	212	
13.	5	1	20	0.53:0.52:0.23:1	2.30	1.02	95	42	0.23	285	$CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $AlPO_4$
14.	5	1	40	0.55:0.54:0.28:1	1.94	1.00	99	70	0.29	252	
15.	5	1	60	0.50:0.55:0.62:1	0.81	0.91	108	66	0.34	263	+ amorphous phase
16.	5	2	20	0.38:0.75:0.13:1	2.96	0.50	113	92	0.16	199	$CaHPO_4 \cdot 2H_2O$, $CaHPO_4$,
17.	5	2	40	0.40:0.80:0.13:1	3.16	0.50	96	38	0.14	217	$AlPO_4$, $CaCO_3$ + amorphous
18.	5	2	60	0.57:0.38:0.03:1	18.87	1.48	120	47	0.19	238	phase
19.	8	0.5	20	0.73:0.40:0.48:1	1.52	1.82	140	101	0.74	199	Amorphous phase
20.	8	0.5	40	0.76:0.41:0.55:1	1.37	1.84	142	86	0.55	236	
21.	8	0.5	60	0.89:0.50:0.74:1	1.19	1.78	126	118	0.50	252	
22.	8	1	20	0.57:0.63:0.50:1	1.14	0.90	120	69	0.33	244	
23.	8	1	40	0.54:0.60:0.77:1	0.70	0.90	108	71	0.53	206	
24.	8	1	60	0.60:0.55:0.50:1	1.09	0.91	137	62	0.36	223	
25.	8	2	20	0.44:0.93:0.50:1	0.87	0.48	118	90	0.37	226	$CaHPO_4 \cdot 2H_2O$, $CaCO_3$
26.	8	2	40	0.38:0.81:0.31:1	1.23	0.47	119	45	0.21	198	+ amorphous phase
27	8	2	60	0.43:0.91:0.36:1	1.20	0.47	124	72	0.37	212	$CaHPO_4$, $CaCO_3$ + amorphous phase

Three-level $3^{(k-p)}$ fractional factorial design.

precipitation, sintering, evaporation or oxidation [16]. Numerous methods have been developed for the preparation of aluminium phosphate [8,17–19] including the precipitation methods [8–11]. Burrell et al. [10] pointed out the difficulties that are encountered in obtaining of aluminium phosphates with repeatable properties.

Depending on the molar ratio of $Ca^{2+}:PO_4^{3-}$, pH and temperature, the following phosphates can be obtained: hydrated dicalcium phosphate – $CaHPO_4 \cdot H_2O$, monetite – $CaHPO_4$, octacalcium phosphate – $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, amorphous calcium phosphate – $Ca_3(PO_4)_2$, hydroxylapatite – $Ca_5(PO_4)_3OH$ and tricalcium phosphate – $Ca_3(PO_4)_2$ [20–23].

In this work it was developed a method of preparation of aluminium ammonium calcium phosphates which can be used as the anti-corrosive pigments in binders of solvent-borne polyurethane paints. The obtained materials were characterized in terms of the chemical composition, molar ratio of Al^{3+}/NH_4^+ and Al^{3+}/Ca^{2+}, absorption oil number, specific surface area S_{BET}, pore volume and average particle size.

The parameter characteristic for a given pigment that allows to determine the threshold concentration, is the absorption oil number OA. This number determines the amount of absorbed paraffin oil required for the complete wetting of a pigment particle. This parameter characterizes sorptive properties of a pigment and it depends, among others, on the surface area, material porosity and particle size distribution.

2. Experimental

2.1. Procedure

Studies on the synthesis of aluminium ammonium calcium phosphates were performed on the basis of the experimental planning and analysis according to a three-level $3^{(k-p)}$ fractional factorial design with 27 experiments. The process independent variables were: x_1 – pH of the reaction mixture (5 ± 3), x_2 – molar ratio of $Ca^{2+}:Al^{+3}$ in the substrates (0.5:1, 1:1; and 2:1), and x_3 – process temperature (40 ± 20 °C). Multiple dependent variables defining the physicochemical properties of prepared products were: the molar ratio of Al^{3+}/NH_4^+ (y_1), and Al^{3+}/Ca^{2+} (y_2), oil absorption number (y_3), specific surface area S_{BET} (y_4), pore volume (y_5) and average particle size (y_6).

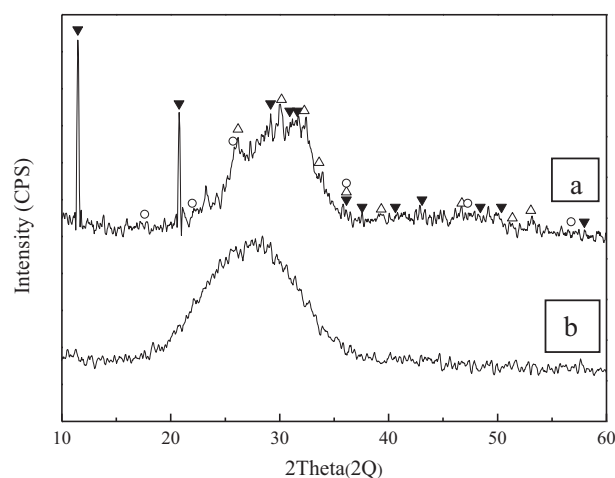**Fig. 1.** X-ray diffraction patterns of aluminium ammonium calcium phosphates produced in reaction: (a) the pH 5, the molar ratio of $Ca^{2+}:Al^{3+}:PO_4^{3-}$ equal to 0.5:0.5:1, temperature 60 °C (experiment 15), (b) the pH 2, the molar ratio of $Ca^{2+}:Al^{3+}:PO_4^{3-}$ equal to 0.31:0.62:1, temperature 20 °C (experiment 1); ▼, $CaHPO_4 \cdot 2H_2O$; △, $CaHPO_4$; ○, $AlPO_4$.

The objective of the experiments performed according to the plan was to determine the fractional factorial 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 expected properties. A factorial plan and the results obtained from the experiments are summarized in Table 1.

2.2. Sample preparation

Reagent grade substrates $AlCl_3$, $CaCO_3$, H_3PO_4 (85 wt%) and aqueous ammonia (25 wt% NH_3) were used. In the experiments the phosphate precipitation process was carried out in a glass reactor for 50 min. The molar ratios of Ca^{2+}:Al^{+3}:PO_4^{3-} in the

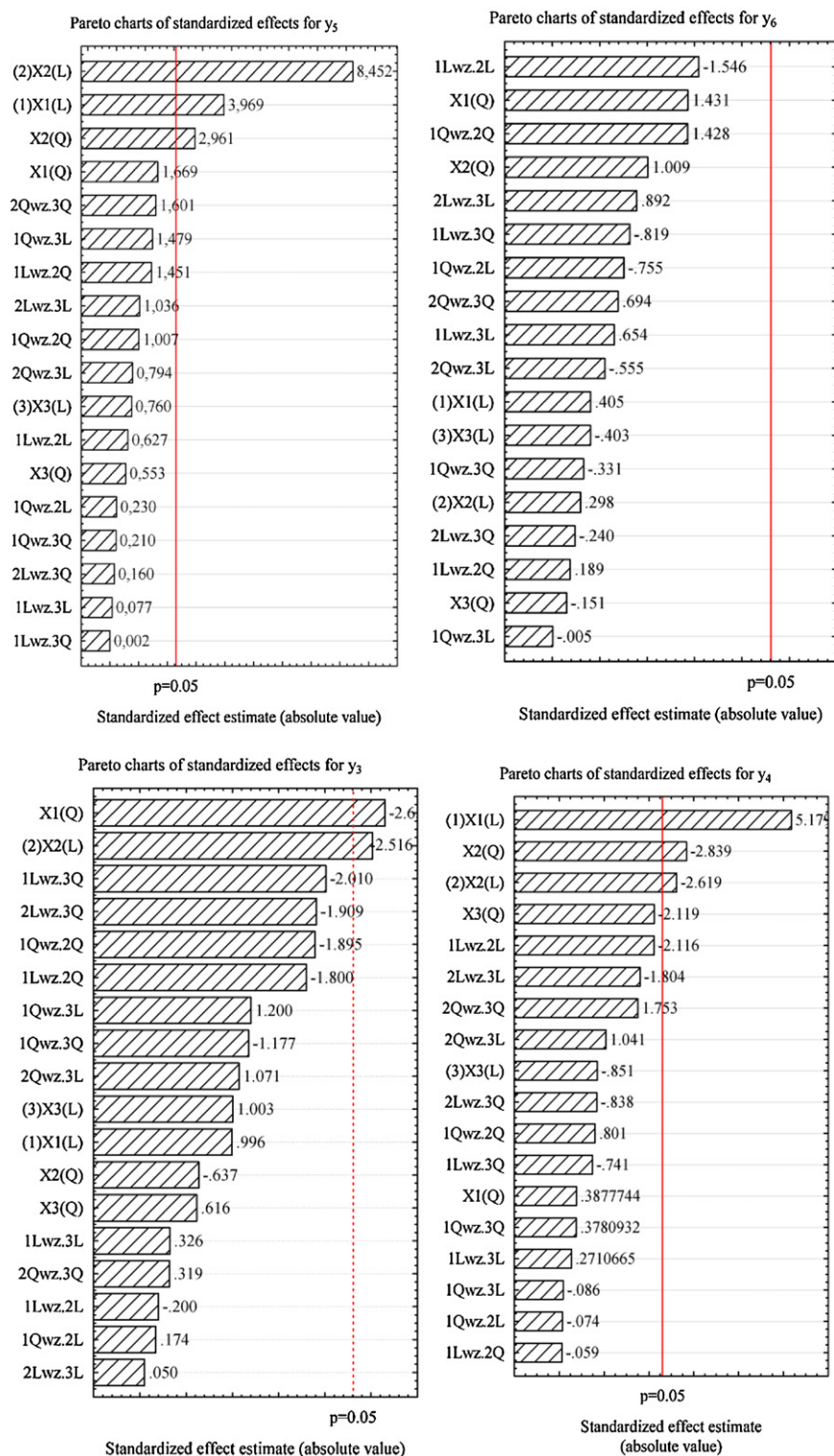Fig. 2. Pareto charts of standardized y_1, y_2, y_3, y_4, y_5, y_6.

Pareto charts of standardized effects for y_1
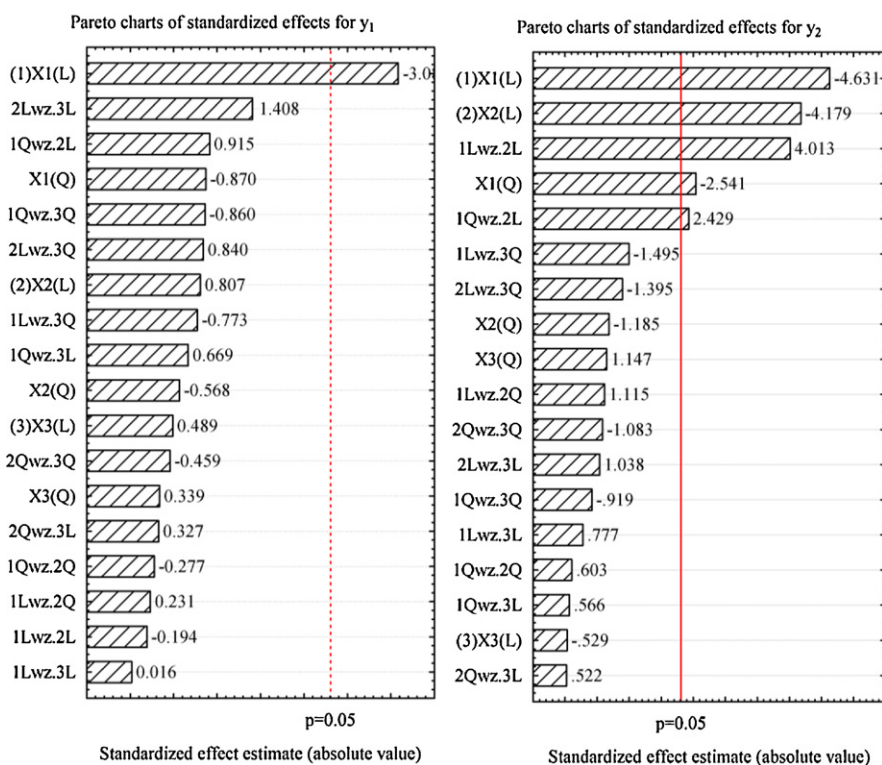

Pareto charts of standardized effects for y_2

Fig. 2. (Continued).

reaction mixture amounted to 0.31:0.62:1; 0.5:0.5:1 and 0.72:0.36:1, pH of the reaction was equal to 5 ± 3, whereas temperature was 40 ± 20 °C. The total concentration of salt amounted to 40 wt%. A solution of aluminium chloride and calcium carbonate was dosed into a phosphoric acid solution over a period of 20 min, while the stirring velocity was constant. The obtained precipitate was separated from the mother liquor using a vacuous filter, followed by triple washing with water (weight ratio of liquid to the solid phase was 3:1). Finally, the obtained product was dried for 3 h at 70 °C.

2.3. Sample characterization

The content of aluminium and calcium in the products was determined by ICP-AES analysis (Optima 5300 DV, Perkin Elmer). The phosphates and ammonium ion contents were determined using spectrophotometric method [23] and potentiometric method [24] ion selective electrode, respectively. The phase composition was studied with X-ray diffraction analysis (X'Pert PRO Philips diffractometer, Cu K_α radiation). The absorption oil number (grams of oil required to form a homogeneous paste with 100 g of tested dry pigment) was determined according to the standard method [25]. BET surface area and the pore volume of phosphates were measured with the use of Micrometrics Quadrasorb SI Quanta-chrome Instrument [ASAP2010 M]. N_2 adsorption/desorption measurements were carried out at liquid N_2 temperature. The average particle size of the materials was determined by laser optic microscopy (Keyence VK-9710k Colour 3D Laser Scanning Microscope).

3. Results and discussion

A phase composition analysis of the materials prepared has demonstrated that both amorphous phosphates and phosphates with a highly differential contribution of the crystalline phases

were obtained. The X-ray diffraction patterns of selected materials are presented in Fig. 1, whereas their characteristics are summarized in Table 1. The compounds such as $CaHPO_4 \cdot H_2O$, $CaHPO_4$, $AlPO_4$ and $CaCO_3$ (Table 1) were observed among the crystalline phases. It was found that unreacted calcium carbonate occurred in the reaction products precipitated from the reaction mixture, for which the molar ratio of calcium to aluminium was the highest and was equal to 2:1. The crystalline phases corresponding to the following phosphate compounds: ammonium aluminium, ammonium calcium, calcium aluminium or aluminium calcium (e.g. $Al(NH_4)_3(PO_4)_2$, $CaNH_4PO_4$, $AlCa(PO_4)_{1.67}$, $AlCa(NH_4)(PO_4)_2$) were not found. Moreover, the above mentioned phosphates may occur in the amorphous phase. All the obtained products contain nitrogen, calcium, aluminium and phosphorus in the various amounts. Therefore, the discussion on the impact of independent variables on the properties of obtained materials focused on aluminium ammonium calcium phosphates.

The studies were carried out for three levels of variance of the input factors. A statistical analysis predestines the approximation of the interactions of process operating variables based on the models with a linear character (L) as well as with a quadratic one (Q). This increases the reliability of evaluation and enables the evaluation of the interactions between the operating parameters [26,27].

A statistical analysis was focused on the determination of the influence of process parameters on the properties of obtained phosphates. The effects of the impact of the extreme values of input factors $x_{1,2,3}$ (independent variables) on the changes of the values of output factors $y_{1,2,3,4,5,6}$ (dependent variables) were evaluated. The results evaluation in the probability test was performed at the significance level equal to 5%.

It was found that PH of the reaction mixture (x_1) had the most statistically significant impact on the value of the molar ratio of Al^{3+}/NH_4^+ (y_1). Taking into account a positive sign of this effect (pH(L), effect 3.39), it was demonstrated that the increase in the x_1 value causes an increase of value of the resultant factor y_1.

Aluminium ammonium calcium phosphates with the highest content of ammonia (the smallest molar ratio of Al^{3+}/NH_4^+) was precipitated from the reaction mixture with pH = 8, at temperature 40 °C when the molar ratio of $Ca^{2+}:Al^{3+}:PO_4^{3-}$ in the reactants amounted to 0.5:0.5:1 (Table 1, experiment 23). The molar ratio of Al^{3+}/NH_4^+ in the obtained products varied in the range from 0.70 to 27.93.

In the statistical evaluation, the molar ratio of Al^{3+}/NH_4^+ and Al^{3+}/Ca^{2+} (y_2) in aluminium ammonium calcium phosphates was dependent on pH of the reaction mixture ($x_1(L)$ effect −6.34; $x_1(Q)$ effect −3.01). However, this interaction had an negative sign. In that case, the increase of the value of independent variable x_1,

resulted in the increase of the value of the resultant factor y_2. In addition, a significant influence of the molar ratio of $Ca^{2+}:Al^{+3}$ in the reactants on this dependent variable ($x_2(L)$, effect −5.72) was observed. In the obtained products, this molar ratio of Al^{3+}/Ca^{2+} was within the range from 0.47 to 24.48. The phosphates with the highest content of calcium in relation to aluminium were precipitated mainly from the reaction mixture with pH = 8 and the molar ratio of $Ca^{2+}:Al^{3+}:PO_4^3$ equal to 0.72:0.36:1 (Table 1, experiments 26 and 27).

By evaluation of the effects of the impact of independent variables on the value of the oil number (y_3) of obtained materials, it was found that a decrease of the reaction pH will cause the
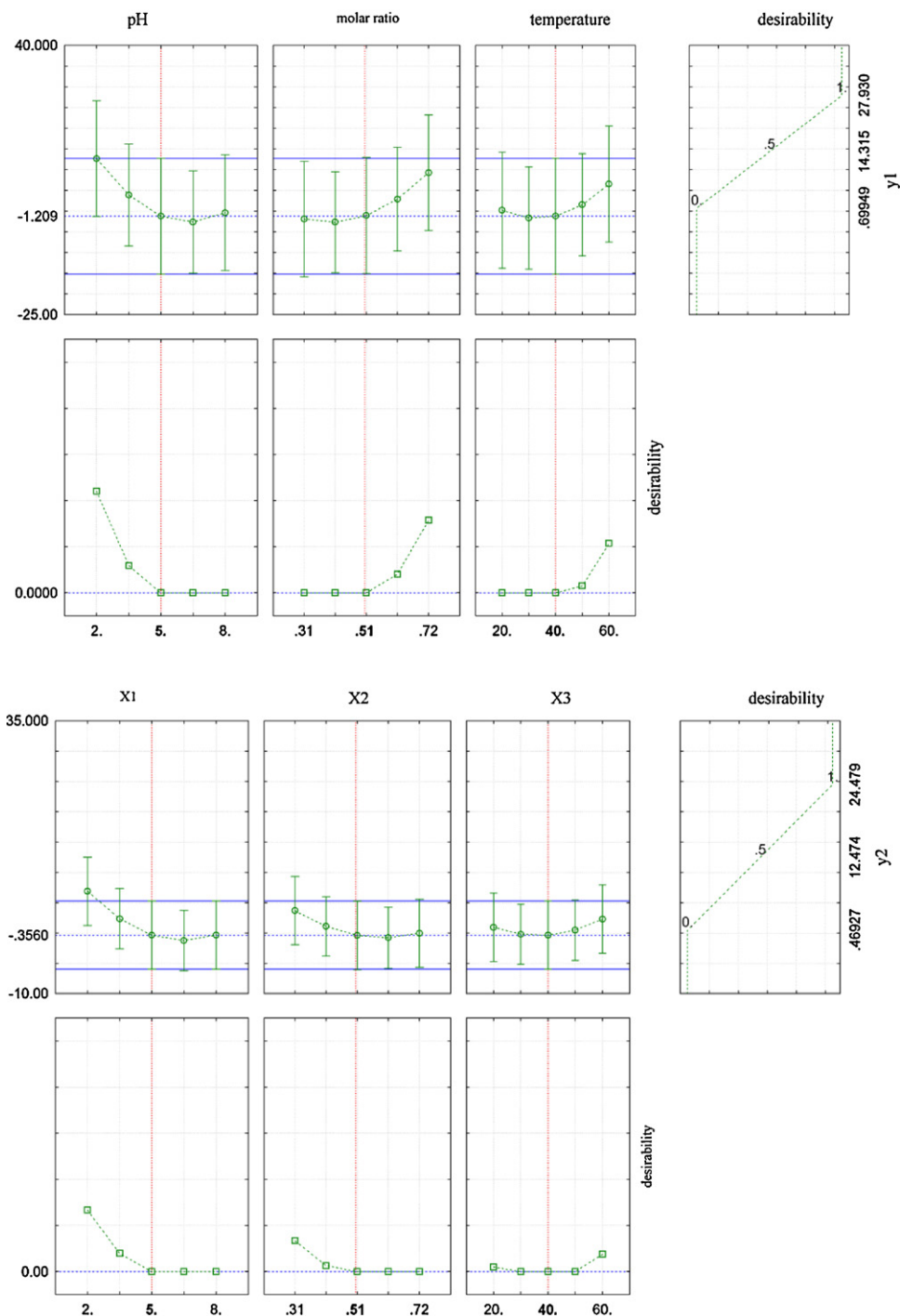

Fig. 3. Profiles for predicted values and desirability y_1, y_2, y_3, y_4, y_5, y_6.
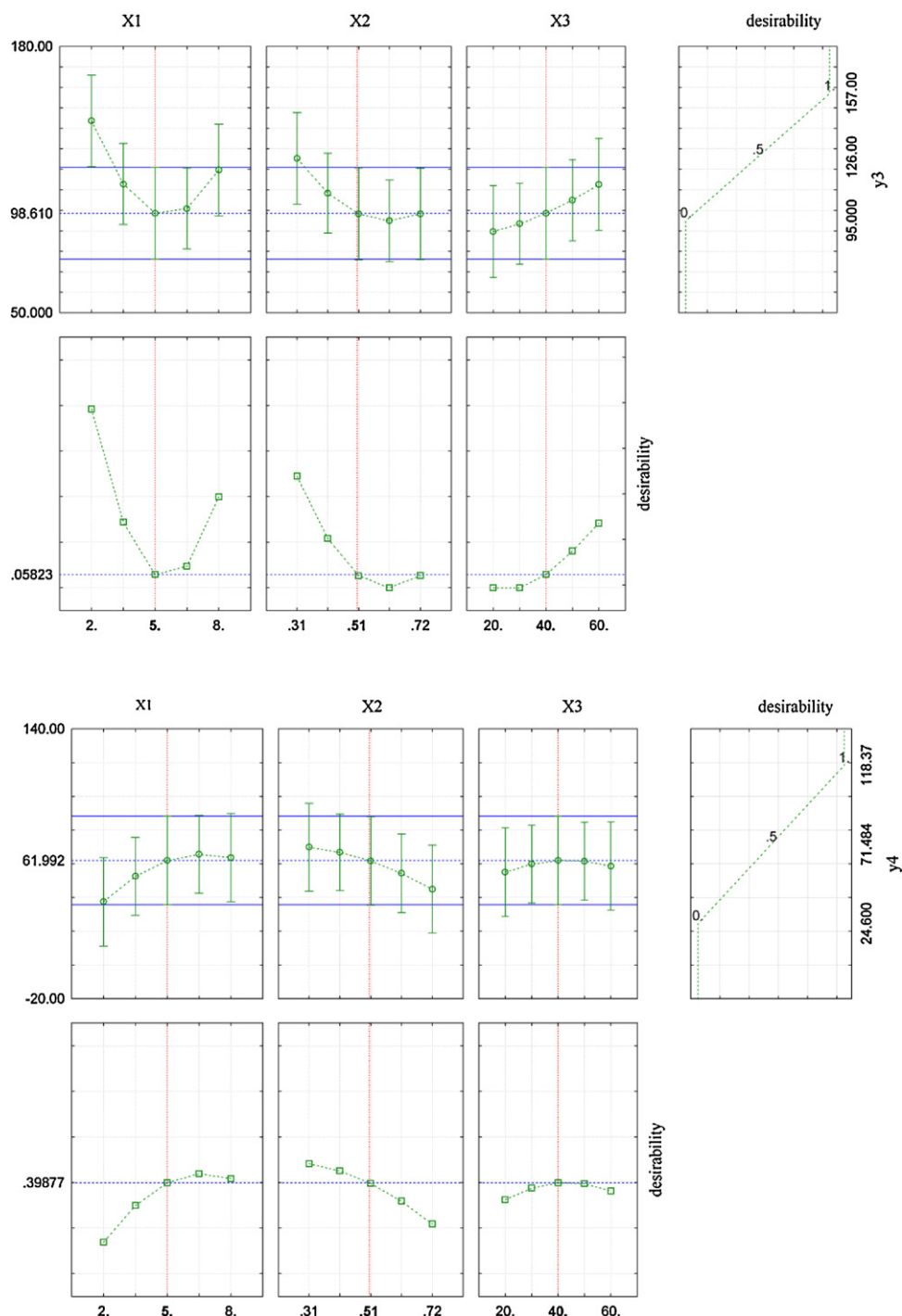
Fig. 3. (Continued).

increase in the value of resultant factor ($x_1(Q)$, effect -12.48). On the other hand, at the highest molar ratio of $Ca^{2+}:Al^{+3}$ in the reactants equal to 2, the value of the product oil number will be the lowest ($x_2(L)$, effect -13.67). The absorption oil number of phosphates was within the range of 95–157 g oil/100 g product. This number is a parameter characterizing the sorption properties of pigment and it is dependent, among others, on the specific surface area and the distribution of particle size.

It was demonstrated that the surface area S_{BET} (y_4) of aluminium ammonium calcium phosphates was affected the most statistically significantly by the interaction of the pH reaction mixture ($x_1(L)$, effect 32.98) and the molar ratio of calcium to aluminium in the reaction mixture ($x_2(L)$, effect -16.67; $x_2(Q)$, effect -15.66). Therefore, materials with the largest specific surface area can be obtained from the reaction mixture with the molar ratio of calcium to aluminium equal to 0.5 and with pH = 8. The surface area of obtained products was within the range from 25 to 118 m^2/g. Aluminium ammonium calcium phosphates which the highest surface area were precipitated from the reaction mixture with pH = 8, when the molar ratio of $Ca^{2+}:Al^{3+}:PO_4^{3-}$ in the reactants amounted to 0.31:0.62:1 at temperature 60 °C (Table 1, experiment 21).
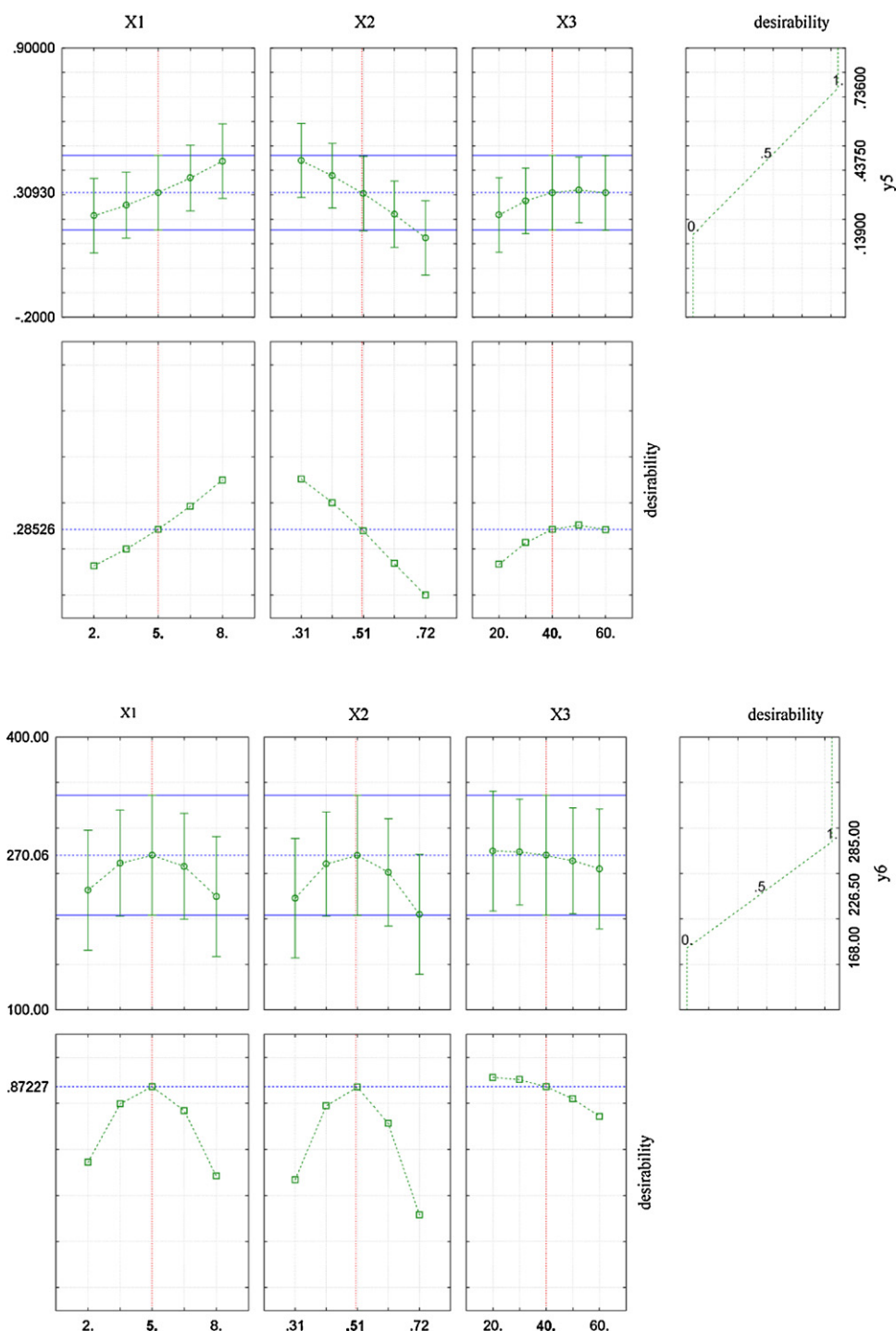
Fig. 3. (Continued).

The specific surface area of materials depends on the particles size, their shape and porosity. The influence of the average particle size and the pore volume on the surface area of prepared phosphates was described by means of a nonlinear model with two independent variables in the following form:

$$z = b_1 + b_2x + b_3y + b_4x^2 + b_5xy + b_6y^2$$

where z is the specific surface area (m^2/g), x is the pore volume (cm^3/g), and y is the average particle size (nm).

The regression dependence was estimated with the utilization of module of the multiple regression by standard method in which all the variables were incorporated into the regression equation (the significance level α – 0.05). A statistically significant interaction (with a square character) of the particle size and pore volume on the surface area has been determined (the square of multiple correlation coefficients equals to $R^2 = 0.74$).

PH of the reaction mixture ($x_1(L)$, effect 0.15) and the molar ratio of Ca:Al in the reactants ($x_2(L)$, effect −0.31; $x_2(Q)$, effect −0.09) also had a statistically significant impact on the pores volume (y_5) of aluminium ammonium calcium phosphates.

In the statistical evaluation of examined model, the reaction temperature did not have a significant influence on the dependent variables y_{1-6}. Nevertheless, this factor can modify the strength of

effect caused by the reaction pH and the molar ratio of calcium to aluminium in the reactants on the molar ratio of Al^{3+}/NH_4^+ and Al^{3+}/Ca^{2+} their absorption oil number, specific surface area, pores volume and particle size. However, a statistically significant impact of independent variables (x_1–x_3) on the average particle size (y_6) of obtained phosphates was not found. This particle size was within the range of 168–285 nm.

Based on the ANOVA method [27], calculations of variance analysis were performed in order to confirm the significance of the obtained effects evaluation. A significant influence of the process pH and the molar ratio of reactants on the dependent variables y_{1-5} was also found in this case.

In accordance with the experimental design, 3 series of studies, each with 9 experiments have been performed. In each series the reaction mixture pH amounted to 2, 5 and 8. Within a given series 3 experiments with assumed molar ratio of Ca^{2+} to Al^{3+} in the reagents, i.e. 0.5, 1 and 2 by changing in them the process temperature (20, 40 and 60 °C) have been performed.

The statistical correctness of the experimental results was evaluated on the basis of the ANOVA method and a graphical data display (Pareto charts) was used (Fig. 2). They present a normalized strength of the effects representing the interactions of studied process factors (independent variable x_1–x_3) on the output factors (dependent variables y_1–y_6). It has been statistically confirmed, that pH of the reaction mixture and molar ratio of Ca^{2+}/Al^{3+} in the substrates influenced on y_2, y_3, y_4 and y_5. The molar ratio of Al^{3+}/NH_4^{3+} in the products was only affected by the first factor (x_1). The particle size of the product was not dependent on the studied process parameters. The physicochemical properties of precipitated phosphates were not also dependent on the process temperature.

The dependent variables predictions, with the presentation of profiles of approximation of the output parameters, with regard to consecutive input variables, were also performed. The profiles of responses usefulness, for the defined values of usefulness of the output parameters (U) were also shown. The input values resulting in the most expected approximated response of the output values y_{1-6} (Fig. 3a–f) were determined on the basis of obtained profile of approximation and the utility function. Such a procedure may be utilized for performing a series of experiments in order to achieve the desirable content of the components as well as their expected absorption oil number, specific surface area, pore volume, and average particle size in the obtained phosphate compounds.

4. Conclusions

It was demonstrated that the molar ratio of Al^{3+} to NH_4 (y_1), Al^{3+} to Ca^{2+} (y_2), absorption oil number (y_3), specific surface area S_{BET} (y_4), and pore volume (y_5) in the products and the remaining dependent variables y_{3-5} were dependent on pH of the reaction mixture (x_1) as well as the molar ratio of calcium to aluminium in the reactants (y_2). A lack of statistically significant impact of the independent variables x_{1-3} on the average particle size of products (y_6) was found.

It was demonstrated that undoubtedly amorphous materials were obtained in the experiments, independently on pH of the reaction mixture and the process temperature. However, only in the cases where the molar ratio of Ca to Al in the reactants was 0.5.

The performed statistical evaluation of experimental design enabled the selection of the process parameters in the direction of obtaining aluminium ammonium calcium phosphates with expected values of examined input parameters, that is, the designed physicochemical properties. In order to obtain phosphates with a high content of aluminium in relation to ammonium and calcium, one should precipitate them from the reaction mixture with low pH. On the other hand, the materials with the largest specific surface area and pore volume should be synthesized from the reaction mixture with high pH and a low molar ratio of calcium to aluminium, respectively 8 and 0.5.

The determination of the approximation profile, that is fitting of the regression equation for the input factors to measured values of the resultant factor enabled to determinate the input parameters values (x_{1-3}), which ensure the achievement of the most desirable (useful) approximated values of the output parameters (y_{1-6}). The responses of input parameters values determined on the basis of the approximation profile and the utility function can be utilized for the realization of a series of experiments, in which a product with desirable value y_{1-6} is obtained.

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