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Magnesium, aluminum, and zinc co-substituted hydroxyapatite: anti-corrosion properties

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Abstract

Purpose – The purpose of this study was to investigate the influence of doping ions Mg$^{2+}$, Zn$^{2+}$, Al$^{3+}$ to the structure of hydroxyapatite (HAP; Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) and subsequently to evaluate their adaptation in structure and their anticorrosive properties.

Design/methodology/approach – The substituted hydroxyapatite was synthesized by precipitation method that included the addition of Mg$^{2+}$, Zn$^{2+}$ and Al$^{3+}$ containing precursors to partially replace Ca$^{2+}$ ions in the hydroxyapatite structure. For precipitation synthesis, three ratios of Ca/P = 1; 1.67; 3 and two values of pH = 7 and 12 were selected. Samples 1 (Ca/P = 1; pH = 7), 2 (Ca/P = 1.67; pH = 7), 3 (Ca/P = 3; pH = 7) and 5 (Ca/P = 1.67; pH = 12) were chosen to monitor the influence of doping ions Mg$^{2+}$, Zn$^{2+}$ and Al$^{3+}$ to the structure of hydroxyapatite and its anticorrosive properties.

Findings – The chosen synthesis conditions are appropriate for the formation of crystalline HAP substituted by elements Mg, Zn and Al. Only for one sample (1-Mg), two different phases (hydroxyapatite and whitlockite) were identified in the phase composition. On the basis of preliminary corrosion tests, pigments were divided into three groups pursuant to their anticorrosion effectivity: pigments with high corrosion-inhibition efficiency; pigments without anticorrosive properties; and pigments that promote corrosion processes.

Originality/value – In addition, no doping effect can be observed except for the sample 1-Mg, which consists of two phases (hydroxyapatite and whitlockite). Preliminary corrosion tests prove that some samples of HAP have extremely high anticorrosive effectivity as effectivity of the commercial pigments. The accelerated corrosion test showed that HAP samples have insufficient corrosion-inhibition properties for coating applications compared with the commercial pigment.

Keywords Corrosion, Inhibitors, Degradation, Corrosion science, Coatings and linings, Hydroxyapatite, Whitlockite, Co-substitution, Preliminary and accelerated corrosion tests, Corrosion

1. Introduction

Pigments based on phosphorus compounds are currently the most significant group of pigments that have acquired the status of “non-toxic” anti-corrosion pigments (Buxbaum and Pfaff, 2005). Phosphates are used as an additive to the formulation of organic coatings of any type, providing easily available, cost-effective and metal protection against atmospheric corrosion. Like other inorganic salts, phosphates are kinetically active corrosion inhibitors that are essentially capable of affecting the rate of the corrosion process. The mechanism of phosphate inhibition consists a number of independent processes (Gorodylova et al., 2016). Owing to the anionic part of phosphate inhibitors, these phosphate species are not themselves red-ox active and therefore are unable to initiate the formation of protective oxidized layers on the metal surface. This requires the contribution of other passivators (hydroxyl or oxygen groups present in the aqueous medium).

In this case, a protective film consisting essentially of metal oxides or hydroxides is formed, while the phosphate anions steady and reinforce the protective oxide layer by the pore closing mechanism. Creating such an intensified passive layer in active corrosion zones reduces the rate of electrochemical reaction or blockades corrosion processes. The closing mechanism is considered to be the main subsidy to the inhibitory activity of phosphates. The occurrence of phosphates in the passive layer structure under the phosphate-containing paint was certified in few studies (Gorodylova et al., 2016; Poledno, 2003). The cationic part of phosphate inhibitors, habitually alkaline earth metals, zinc, strontium and aluminum, does not have important inhibitory activity, nevertheless, it designates the relevant physicochemical properties of pigments such as their solubility and the pH of the environment. The low solubility of the pigment particles may initiate some anticorrosive species to participate in chemical corrosion inhibiting reactions. The pH of the environment influences the kinetics of corrosion reactions and the passivation of the produced product (Gorodylova et al., 2016).

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Anti-corrosion properties
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In recent years, considerable attention has been paid to the use of hydroxyapatite (calcium hydroxyphosphate) in the field of orthopedics, where these phosphates have to replace either partially or completely bone tissue (Rivera-Muñoz, 2011; Gshalaev and Demirchan, 2013). Another application of apatite is its use as a protective coating of marble, adsorbent, and photocatalyst (Huang et al., 2016a; Graziani et al., 2016; Reddy et al., 2007).

One of the most important requirements in using these apatite materials is that interactions may exist in contact with living tissues are not toxic. As a result of friction and wear of HAP, it is necessary to study its mechanical and thermal behaviour. Some studies indicate that HAP stoichiometry plays an important role in mechanical properties. Better results provide a Ca/P ratio of between 1.60 and 1.67, and mechanical strength decreases when grain size exceeds 2 μm. For this reason, the importance of morphology and microstructure control during the synthesis of the HAP process is decisive (Rivera-Muñoz, 2011; Gshalaev and Demirchan, 2013). The structure of HAP can also accept minerals imitating bone material. The addition of bioactively active ions to biochemical material based on HAP structure can increase the biological activity of implants. Especially because of its excellent biocompatibility and osteoconductive, synthetic hydroxyapatite has been extensively studied as a surface material for metallic implants. Hydroxyapatite containing minor groups and elements (e.g. CO3\(^{2-}\), Ca\(^{2+}\), Na\(^{+}\), and Mg\(^{2+}\)) as well as trace elements (e.g. Sr\(^{2+}\), K\(^{+}\), Cl\(^{-}\) and F\(^{-}\)); imitate bone mineral. These smaller groups and elements play an important role in the physiological reactions associated with bone metabolism (Huang et al., 2016b).

The traditional choice of metals for implants has been limited to alloys with good biocompatibility and high corrosion resistance. For example, nowadays, alloys of magnesium, titanium, and zinc are used as an implant material. Magnesium and its alloys have importance for biomedical applications owing to their hopeful biocompatibility and degradability in living beings. In addition to biocompatibility, they have further advantages such as low density, high specific strength, high thermal conductivity and corresponding hardness (Mensah-Darkwa et al., 2013). The use of magnesium as an implant material is restricted due to its fast corrosion in the occurrence of body fluids, which results in rapid release of undesirable corrosion products. This can lead to the production of gaseous hydrogen and alkalinizing body fluid that can suppress wound healing and to necrosis of the ambient tissue. In small amounts, these corrosion products can be metabolized in vivo (Mensah-Darkwa et al., 2013; Dunne et al., 2016). To use magnesium as an effective implant, the range of magnesium rust must be decelerated. Surface coating materials that reduced corrosion rates and meliorate the mechanical and biological properties of magnesium and its alloys involve a HAP-based coating because its chemical and crystallographic structure is like to bone (Mensah-Darkwa et al., 2013).

Very interesting is the substitution of Zn\(^{2+}\) ions to the structure of hydroxyapatite due to its occurrence in biological tissues and its multiple roles in biological functions. It has been demonstrated that involving Zn\(^{2+}\) ions into implants can support metabolism and bone growth, improve bone density and aver bone loss (Livitska et al., 2016).

2. Experimental parts

2.1 Materials

Ca(NO\(_3\))\(_2\)-4H\(_2\)O (98 per cent, Lachema, Czech Republic), (NH\(_4\))\(_2\)HPO\(_4\) (98 per cent, Lachema, Czech Republic), NH\(_4\)OH (25 per cent, Penta Chrudim, Czech Republic), Al(NO\(_3\))\(_3\)-9H\(_2\)O (99.9 per cent, Sigma Aldrich, Germany), Mg(NO\(_3\))\(_2\)-6H\(_2\)O (99 per cent, Lachner, Czech Republic), Zn(NO\(_3\))\(_2\)-6H\(_2\)O (99 per cent, Lachema, Czech Republic) were used for precipitation method. For the synthesis of hydroxyapatite, solutions for starting materials (Ca(NO\(_3\))\(_2\)-4H\(_2\)O, (NH\(_4\))\(_2\)HPO\(_4\)), Al(NO\(_3\))\(_3\)-9H\(_2\)O, Mg(NO\(_3\))\(_2\)-6H\(_2\)O and Zn(NO\(_3\))\(_2\)-6H\(_2\)O of 1 mol/l were prepared. The precise concentrations of these solutions were determined using analytical methods.

2.2 Chemical analysis of starting materials

Determination of calcium concentration was performed by a chelating method using Eriochrome black T as an indicator (Šimková et al., 2018). Phosphorus concentration was resolved by the photometric method (Pribil, 1961). Magnesium and zinc concentration was decided by the chelating method using Eriochrome black T (Mg) and xylenol orange as an indicator (Pribil, 1961; Záruba, 2016). Determination of aluminum was performed by gravimetric method (Sommer, 1995).

2.3 Synthesis of HAP

To choose the appropriate synthesis conditions for the formation of doped HAP, thermodynamic stability of pure HAP phase in aqueous solution was analyzed and approved in laboratory conditions (Hermassi et al., 2015). Figure 1 shows the predominance area diagram for the Ca\(^{2+}\)-PO\(_4\)^{3-}\) water system at 25°C. It is obvious that hydroxyapatite is stable in the pH range from 4.8 to 14. Owing to this information, three Ca/P ratios were chosen for the synthesis of hydroxyapatite, which was studied at pH = 7 and pH = 12 based on the area of the hydroxyapatite form:

Ca/P = 1. In this case, hydroxyapatite formation occurs in excess of phosphate ions.
Ca/P = 1.67. This ratio corresponds to the Ca/P stoichiometry of hydroxyapatite.
Ca/P = 3. Hydroxyapatite formation occurs in excess of calcium ions.

This work is focused on the influence of doping of Mg, Zn and Al elements to the structure of hydroxyapatite and subsequently to evaluate their adaptation in structure and their anticorrosive properties. Samples were prepared by the precipitation method. Three ratios of Ca/P = 1; 1.67 and 3 were selected; two pH ranges of 7 and 12, where ammonia hydroxide solution was used to adjust the pH and precipitation rate of 2 ml/min. Based on the crystal size results from the previous study (Šimková et al., 2018), when the SEM and XRD analysis proved the comparability between the minimum dimensions from the SEM images and the maximum dimensions from the XRD, samples 1 (Ca/P = 1; pH = 7), 2 (Ca/P = 1.67; pH = 7), 3 (Ca/P = 3; pH = 7) and 5 (Ca/P = 1.67; pH = 12) were selected for doping chosen ions (magnesium, zinc, and aluminum). The pigments were analyzed for particle size distribution, crystal size and morphology, phase composition and corrosion tests (preliminary and accelerated).
Samples 1 (Ca/P = 1; pH = 7), 2 (Ca/P = 1.67; pH = 7), 3 (Ca/P = 3; pH = 7) and 5 (Ca/P = 1.67; pH = 12) were selected for doping magnesium, zinc and aluminum ions. A total of 12 samples were prepared containing 0.5 mole of a substituted element under different synthesis conditions. Samples of the series 1 were substituted with Mg2+, Zn2+ and Al3+ ions at the ratio (Ca + M)/P = 1 for M = Mg2+ and Zn2+ and 0.975 for M = Al3+ (precipitation rate of ammonium phosphate monohydrate 2 ml/min, pH = 7). Samples of the 2 series were replaced by Mg2+ and Zn2+ ions at a ratio of (Ca + M)/P = 1.67 and 1.625 for Al3+ ions (precipitation rate of ammonium phosphate monohydrate 2 ml/min, pH = 7). Samples of the series 3 were supplanted with Mg2+ and Zn2+ ions at a ratio (Ca + M)/P = 3 and 2.96 for Al3+ ions under the same precipitation conditions. In the case of samples 5, the ratio (Ca + M)/P = 1.67 for ions Mg2+ and Zn2+ and 1.625 for ions of Al3+ was chosen at the same precipitation rate but at different pH = 12.

The selected suitable precipitation conditions (Ca/P ratio; pH, precipitation speed) were adapted for the synthesis of doped HAP (Table I; precipitation speed 2 ml/min). For the synthesis of the samples, 1 M solutions of the starting compounds (Ca(NO3)2·4H2O, Al(NO 3)3·9H2O, Mg(NO 3)2·6H2O, Zn(NO 3)2·6H2O, (NH4)H2PO4) were prepared. The exact concentration of these solutions was determined using analytical methods (titration, photometric and gravimetric analyses). The obtained precipitates were aged for 24 hours, filtered and washed with distilled water to neutral pH, then dried at 80°C for 6 hours (Figure 2). Analysis of the prepared samples was performed on an optical microscope (Dino-Lite Rack - MS 34 B, AnMo Electronics, Taiwan) directly after precipitation and in 2 and 24 h of aging. Particle size measurement was performed before and after aging (Mastersizer 2000 MU, Malvern Instruments Ltd., UK; Mie approach). The phase composition of the dried samples was analyzed on the benchtop X-ray diffraction instrument (Rigaku MiniFlex 600, Japan).

Preliminary and accelerated corrosion tests of the prepared powders were performed to verify their corrosion inhibition activity. Preliminary corrosion tests include the following: determination of pH and resistivity of aqueous suspensions of pigments (10 per cent), gravimetric determination of weight loss of steel plates, and determination of corrosion indicators for the steel plates after being dipped into pigment extracts for two months and the change of pH and resistivity during this process. The formed corrosion products were analyzed using optical microscope and their phase composition was determined by XRD analysis. Next, for accelerated corrosion tests, samples were dispersed in water-based primer paint and applied on steel substrates (approx. 22 ± 0.1 cm) and tested in corrosion testing chambers (periodic wet-dry exposure to 100 per cent humidity with addition of 0.2 dm3 of SO2 gas at 38°C, Hydrotherm 519, Erichsen, Germany) during three weeks. The thickness of the dried paint coatings was controlled using a coating thickness gauge (Surfacer T1, Phynix, Germany). The color change of the paint samples during the corrosion tests was measured using spectrophotometer (ColorQuest XE, HunterLab, USA). The evaluation of the degradation of the coatings was carried out with respect to the degree of rusting, blistering, cracking, flaking, and delamination according to ISO standards. Evaluation of the degree of corrosion on steel surface was carried out after removal of the paint using NaOH solution (30 Wt.%). Corrosion defects were also analyzed using an optical microscope. The commercial pigments ZP-10 (mixture Zn3(PO4)2·2H2O and ZnO; France) and Zn-Bs-M (Zn3(PO4)2·2H2O and ZnO; France) were used in parallel with the synthesized samples.

**Table I: Overview of the obtained samples and the synthesis conditions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (Ca + M)/P</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca36(PO4)6(OH)2</td>
<td>1</td>
</tr>
<tr>
<td>1-Mg</td>
<td>Ca35Mg0.5(PO4)6(OH)2</td>
<td>1</td>
</tr>
<tr>
<td>1-Zn</td>
<td>Ca29Zn0.5(PO4)6(OH)2</td>
<td>1</td>
</tr>
<tr>
<td>1-Al</td>
<td>Ca25Al0.5(PO4)6(OH)2</td>
<td>0.975</td>
</tr>
<tr>
<td>2</td>
<td>Ca30(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>2-Mg</td>
<td>Ca29Mg0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>2-Zn</td>
<td>Ca28Zn0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>2-Al</td>
<td>Ca25Al0.5(PO4)6(OH)2</td>
<td>1.625</td>
</tr>
<tr>
<td>3</td>
<td>Ca30(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>3-Mg</td>
<td>Ca30Mg0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>3-Zn</td>
<td>Ca29Zn0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>3-Al</td>
<td>Ca25Al0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>5</td>
<td>Ca30(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>5-Mg</td>
<td>Ca29Mg0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>5-Zn</td>
<td>Ca28Zn0.5(PO4)6(OH)2</td>
<td>1.67</td>
</tr>
<tr>
<td>5-Al</td>
<td>Ca25Al0.5(PO4)6(OH)2</td>
<td>1.625</td>
</tr>
</tbody>
</table>
basis of Mie scattering. The measurement is taken in three steps, and results are automatically calculated as average and presented as \(d_{10}, d_{50}\) and \(d_{90}\) values.

2.4.3 **X-ray diffraction analysis**

The phase analysis of the powdered materials was studied by X-ray diffraction analysis (XRD). The phase composition was determined using diffractometer MiniFlex 600 with a vertical goniometer of 17 cm in the \(2\theta\) range of 10°–50°. The accuracy of goniometer was ±0.02°. X-ray tube with Cu anode (\(U = 40\) kV, \(I = 15\) mA) was used (CuKα radiation).

3. **Results and discussion**

3.1 **Optical microscope**

All prepared powders, in which a portion of Ca\(^{2+}\) ions was substituted by Mg\(^{2+}\), Zn\(^{2+}\) or Al\(^{3+}\) ions, were studied by the digital optical microscope. To monitor how the morphology of the samples changed because of aging, the samples were measured immediately after precipitation (**Figure 3a**) and 24 h after aging (**Figure 3b**).

According to optical microscopy results, the doped HAP formed as agglomerates of small crystallites of different size and

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**Figure 2** Flow chart for the synthesis of HAP by precipitation process

**Figure 3** The standard appearance of samples 1-Mg, 1-Zn and 1-Al (ratio Ca/P = 1; \(pH = 7\); 2 ml/min) measured directly after precipitation (a) and after 24 h aging (b)
shape similar to the pure HAP samples. Owing to the very small percentage of the content of doped elements, it was assumed that the size and shape of crystallites of doped samples are similar to not modified HAP. In particular, under the chosen conditions, HAP phase forms as nanocrystalline which size and shape depend on the Ca/P ratio (with Ca/P = 1 form needle-like crystallites, with Ca/P = 1.67 – thin plates, with Ca/P = 3 – needle-like, thin plates and bulk crystallites), pH (with pH = 7 from larger and thinner crystallites, with pH = 12 - smaller and bulk crystallites), does not depend on the precipitation speed. Particle size measurements of the samples showed the values of $d_{50}$ in ranged from 13.18 to 20.42 $\mu$m. These values indicate the size of agglomerates, which are slightly larger than the values for not-doped HAP samples.

3.2 Particle size distribution

Particle size distribution of synthesized samples was measured after 24 h aging with the Mastersizer 2000 MU. Signal was evaluated by Mie scattering. The distribution curves and $d_{10}$, $d_{50}$, $d_{90}$ and distribution span were obtained. Figure 4 shows the summary of volume distribution curves of unmodified and doped samples 1, 2, 3 and 5.

From the distribution curves of sample 1 (Figure 4a), it is clear that the sample of unmodified hydroxyapatite has a distribution curve shifted to lower values compared to modified HAP. The highest mean value of $d_{50}$ showed a sample of hydroxyapatite substituted with Mg$^{2+}$ ions (Table II). For sample 2 (Figure 4b), it is clear that the sample of pure HAP has the lowest particle size values. The mean particle size $d_{50}$ is less than 10 $\mu$m, while the Mg$^{2+}$, Zn$^{2+}$ and Al$^{3+}$ ions lead to an increase in $d_{50}$ to 10-20 $\mu$m. The distribution curves for samples 3 (Figure 4c) are almost comparable, however, the modified Zn$^{2+}$ ions exhibit the highest $d_{50}$ value (Table II). Samples 5 provide significantly wider distribution curves (Figure 4d). The pure hydroxyapatite of sample 5 gave the lowest $d_{50}$ value and also the lowest distribution width. In contrast, the highest $d_{50}$ value, as well as the $d_{10}$ and $d_{90}$ values, was measured at the sample containing the Al$^{3+}$ ions. Table II also shows that, in the case of samples substituted Mg$^{2+}$ ions, there is a context between the ratio $(\text{Ca} + \text{M})/\text{P}$ and the mean particle size values, respectively agglomerates. If the ratio increases, the mean values are reduced.

**Figure 4** Distribution curves of doped samples 1, 2, 3 and 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{10}$ [$\mu$m]</th>
<th>$d_{50}$ [$\mu$m]</th>
<th>$d_{90}$ [$\mu$m]</th>
<th>Span</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Mg</td>
<td>13.72</td>
<td>25.15</td>
<td>44.67</td>
<td>1.23</td>
</tr>
<tr>
<td>1-Zn</td>
<td>5.61</td>
<td>14.25</td>
<td>29.27</td>
<td>1.66</td>
</tr>
<tr>
<td>1-Al</td>
<td>7.62</td>
<td>15.89</td>
<td>28.97</td>
<td>1.34</td>
</tr>
<tr>
<td>2-Mg</td>
<td>7.50</td>
<td>16.09</td>
<td>29.98</td>
<td>1.40</td>
</tr>
<tr>
<td>2-Zn</td>
<td>6.53</td>
<td>14.04</td>
<td>26.07</td>
<td>1.39</td>
</tr>
<tr>
<td>2-Al</td>
<td>7.51</td>
<td>17.49</td>
<td>38.37</td>
<td>1.76</td>
</tr>
<tr>
<td>3-Mg</td>
<td>4.96</td>
<td>11.67</td>
<td>23.49</td>
<td>1.59</td>
</tr>
<tr>
<td>3-Zn</td>
<td>8.49</td>
<td>17.24</td>
<td>32.26</td>
<td>1.38</td>
</tr>
<tr>
<td>3-Al</td>
<td>4.86</td>
<td>13.18</td>
<td>29.09</td>
<td>1.84</td>
</tr>
<tr>
<td>5-Mg</td>
<td>6.55</td>
<td>15.56</td>
<td>45.73</td>
<td>2.52</td>
</tr>
<tr>
<td>5-Zn</td>
<td>6.41</td>
<td>15.70</td>
<td>42.01</td>
<td>2.27</td>
</tr>
<tr>
<td>5-Al</td>
<td>9.48</td>
<td>20.42</td>
<td>54.01</td>
<td>2.18</td>
</tr>
</tbody>
</table>
3.3 X-ray diffraction analysis
The phase composition of the samples was determined by XRD analysis. According to XRD analysis, most samples showed a single phase composition of HAP (hexagonal or monoclinic Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, Figure 5). Only one sample – 1-Mg – consists of two phases: hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ with the parameters: monoclinic crystalline system; spatial group P2$_1$/b and whitlockite Ca$_{18}$Mg$_2$H$_2$(PO$_4$)$_{14}$ with parameters: rhombohedral crystalline system; space group R$_3$C (Figure 6). Because only the HAP phase has been identified in other doped samples, it is clear that doping elements Mg, Zn, and Al occupy the calcium positions in the crystal structure of HAP. This can be expected because the atom radius of these elements are approximately same to or smaller than the radius of Ca (r (Ca$^{2+}$) = 0.106 nm (c.n.7), r (Mg$^{2+}$) = 0.089 nm (c.n. 8), r (Zn$^{2+}$) = 0.09 nm (c.n. 8), r (Al$^{3+}$) = 0.0535 nm (c.n. 6)).

Because only the HAP phase has been identified in other doped samples, it is clear that doping elements Mg, Zn, and Al occupy the calcium positions in the crystal structure of HAP. This can be expected because the atom radius of these elements are approximately same to or smaller than the radius of Ca (r (Ca$^{2+}$) = 0.106 nm (c.n.7), r (Mg$^{2+}$) = 0.089 nm (c.n. 8), r (Zn$^{2+}$) = 0.09 nm (c.n. 8), r (Al$^{3+}$) = 0.0535 nm (c.n. 6)).

The crystal size was calculated from the diffractogram based on the diffraction line width using the Scherrer equation, Williamson–Hall (WH) (Kalita and Kalita, 2017) and the Halder–Wagner (HW) method (Motevalizadeh et al., 2014). Based on the XRD patterns, i.e. XRD reflection width, the crystallite size of the powders was also calculated (Table III). The size of the crystallites of doped HAP is in the range of 2.81-49.2 nm according to the results based on Scherrer equation, 5.3-7.1 nm – the Hall–Wagner method, and 5.9-10.6 nm – the Williamson–Hall method. The large difference in crystallite size which was calculated according to the Scherrer equation can be explained by the large difference of the crystal dimensions.

Figure 5 (a) Diffractogram of sample 1 (hexagonal HAP); (b) diffractogram of sample 2 (monoclinic HAP)

Figure 6 The diffraction pattern of the sample 1-Mg
general, crystallites of doped samples are slightly smaller than for pure HAP.

3.4 Corrosion tests
3.4.1 Preliminary corrosion test
Preliminary corrosion tests do not evaluate visible changes in samples that have resulted from a corrosion test, but the value associated with the process of degradation of organic coatings is measured. These tests include determination of pH and resistivity of aqueous suspensions of pigments (10 per cent), gravimetric determination of weight loss of steel plates, and determination of corrosion indicators for the steel plates (Myšková, 2014; Mojžíš, 1967). Measurement of pH and resistivity of aqueous suspensions of pigments is intended to analyze the corrosive environment of pigments. The pH value in the range 7-9 is generally considered to be optimal for the best performance of anticorrosion pigments. Phosphate anticorrosion pigments show high efficiency in a slightly acidic pH range. Resistivity is an indicator of the concentration of dissolved ions in suspension, which are formed in the result of the hydrolysis of pigment and may participate in the corrosion inhibition processes. This means that the resistivity of the aqueous pigment suspensions is an indicator of the solubility of the pigment in water. The partial solubility of pigment particles is very important for the effectiveness of anticorrosive phosphate pigments. Figure 7 shows change of pH and conductivity of the pigment suspensions during 28 days of aging.

The measured values present that the hydrolysis of the pigment ions supports the formation of acid species, leading to decrease of pH. The conductivity of the samples was very different, but in general, it increased indicating that the concentration of dissolved ions has increased over time. The aqueous suspensions of the pigments were filtered and the pigments extracts were used for the assessment of weight loss of steel plates, which were submerged to extracts for three months. During the test, a different color change of the extracts was observed because of the release of corrosion products (Figure 8). At the same time, the significant increase in pH also indicated intense corrosive processes (cathodic reaction leads to release of hydroxyl species: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$). However, for all samples, the conductivity value reduced. This means that the dissociated ions from the pigment extract have been involved in the formation of a protective layer on the steel surface or other solid products.

Next, corrosion indicators were calculated on basis of corrosion losses of steel plates. Figure 9 shows a relative corrosive decrease for all tested samples. In this case, the water loss is a standard appropriate to 100 per cent.

On basis of the performed tests, the samples can be divided into 3 groups according to their anticorrosion efficiency.

First group – pigments with high anticorrosive efficiency: Corrosion processes in the pigment extracts have been decelerated owing to sufficient concentration of phosphates that inhibit corrosion processes (supported by the mild conductivity values and the formation of Vivianite Fe$_3$(PO$_4$)$_2$$\cdot$8H$_2$O on steel surface). A sample of 1-Mg (Ca$_9$Mg$_{0.5}$(PO$_4$)$_6$(OH)$_2$) from this group demonstrated the best anticorrosive properties, which may be related to phase composition (Whitlockite phase may be more effective for corrosion protection than hydroxyapatite). This group contains mainly of the samples of series 1 which are formed from powders (supported by low conductivity values and formation of Fe(OH)$_3$ as the main corrosion product). This group includes the samples of series 5.

The second group – pigments without anticorrosive properties: The concentration of phosphate in these extracts is deficient for high anticorrosion efficiency (supported by low conductivity values and formation of Fe(OH)$_3$ as the main corrosion product). This group includes the samples of series 5.

The third group – pigments that support corrosion processes: In this case, the corrosion processes were very intensive because of...
the intensive reaction between the pigment extracts and the steel plate (supported by the very high conductivity values, substantial surface corruption and the formation of FeO(OH)). Such behaviour can be explained by the occurrence of some hydrated complexes of calcium or doping elements, which operate as catalysts for corrosion. This group incorporates the samples of series 2 and 3.

3.4.2 Accelerated corrosion test
Accelerated laboratory tests expedite the corrosion processes on the exposed samples, resulting in rapid corrosion changes on the metal substrate as well as on the organic coating. For the accelerated corrosion tests, samples 1, 1-Mg, 1-Zn, 1-Al, 2, 3, 5 and ZP-10 were selected. These selected pigments were dispersed in the alkyd primer paint. The change in the appearance of the corrosion coatings was obvious visually. The images of all selected samples after the corrosion test are demonstrated in Figure 10. Some samples showed visually more yellow corrosion products (samples 2 and 3), some less (sample 1, 1-Mg, 1-Zn, 1-Al, 5) and the best visual appearance showed a commercial pigment (ZP-10). However, these coloring may be induced by diffusion of corrosion products from the edges of steel sheets, with corrosive stains being very visible.

Examples of coating degradation for the selected samples are revealed in Figure 11. The assessment of the degradation of the coatings after the accelerated corrosion test showed that under the given conditions, the best corrosion properties exhibit sample 5 and the worst is sample 3. The least damaged sample is the ZP-10 (commercial pigment). This result consents with the color change of the samples where for the most damaged sample was determined the highest color difference. For all tested HAP samples, the formation of small crystals on the coating surface was observed (Figure 11). XRD analysis of these crystals identified only organic compounds in their phase composition, which suggests the destruction of the coating. Therefore, based on the accelerated corrosion test, HAP samples showed insufficient corrosion properties for coating applications in collation to standard pigment (ZP-10).

The evaluation of the degradation of the coatings after the accelerated corrosion test was performed with respect to the degree of rusting, blistering, cracking and flaking. Evaluation of the degree of delamination and corrosion in the vicinity of the cut and on the surface was executed after elimination of the coating. All results are shown in Table IV. The appearance of the surface of the steel sheets after paint removal is demonstrated in Figure 12. The evaluation of paint degradation and corrosion on the steel surface was made according to international norms (CSN ISO 8407, 1995; CSN ISO 6270-1, 2002; CSN ISO 3231, 1998; CSN ISO 4628-1, 2004; CSN ISO 4628-2, 2004; CSN ISO 4628-3, 2004;
The rusting was evaluated as a percentage of rust. The quantity (density) and size of blistering were assessed using image standards. Classification and density of cracking were judged using image standards. The appraisal of the degree of corrosion in the vicinity of the cut was evaluated as the width of the corrosion products. The surface corrosion was evaluated as a percentage of the corroded area to the whole area.

In general, the lowest degree of rusting, blistering, cracking and corrosion was observed for sample ZP-10. The results show that under the given conditions sample 5 proves better corrosion properties and sample 3 the worst corrosion properties. The wicked corrosion properties of sample 3 in the accelerated corrosion tests consent with the results of the change in appearance of the paint and preliminary corrosion tests. For other samples, there is no context between the result of preliminary and accelerated corrosion tests.

### 4. Conclusions

On basis of the obtained results, it can be concluded that the chosen synthesis conditions are appropriate for the formation of crystalline HAP substituted by elements Mg, Zn and Al. Only for one sample (1-Mg), two different phases (hydroxyapatite and whitlockite) were identified in the phase composition. Therefore, in other cases, the elements occupy the positions of calcium in the crystal structure of HAP. On basis of preliminary corrosion tests, pigments were divided into 3 groups pursuant to their anticorrosion effectivity: pigments with high corrosion inhibition efficiency; pigments without anticorrosive properties; pigments that promote corrosion processes. It was also shown that the anti-corrosion efficiency of the prepared samples is connected with precipitation conditions. The best anticorrosion efficiency demonstrates the samples of needle-like crystallites of smallest size (series 1). In addition, no doping effect can be observed except for the

### Table IV  Evaluation of paint degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rusting [%]</th>
<th>Blistering (quantity and size)</th>
<th>Cracking (classification and quantity)</th>
<th>Corrosion of steel In the vicinity of the cut [mm]</th>
<th>Corrosion of steel On the surface [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>–</td>
<td>3:1</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>1-Mg</td>
<td>0.5</td>
<td>–</td>
<td>3:1</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>1-Zn</td>
<td>0.05</td>
<td>2-2(S4)</td>
<td>1:;</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>1-Al</td>
<td>0.05</td>
<td>–</td>
<td>1:;</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>–</td>
<td>1:;</td>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>1-2</td>
<td>2-2(S3)</td>
<td>3:2</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>1-2</td>
<td>–</td>
<td>1:;</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>ZP-10</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 11  Appearance of steel sheets of all tested samples after an accelerated corrosion test

![Figure 11](image1)

Figure 12  Appearance of samples after paint removal

![Figure 12](image2)
sample 1-Mg, which consists of two phases (hydroxyapatite and whitlockite). Preliminary corrosion tests prove that some samples of HAP have very high anticorrosive effectiveness as effectiveness of the commercial pigments. The accelerated corrosion test showed that HAP samples have insufficient corrosion inhibition properties for coating applications compared to the commercial pigment. The poor corrosion properties of the pigments in the coating may be related to their low compatibility with the coating, which could be solved by surface modification of the pigment.

### References


ČSN ISO 8407 (03 8102) (1995), Koroze kovů a slitin odstranění korozních zpldin ze vzorků podrobených korozním zkouškám.


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### Anti-corrosion properties

**Lenka Šimković and Petra Sulcová**

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Further reading

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