

# APPLICATION OF DOPED HYDROXYAPATITE AS A CORROSION INHIBITOR

Lenka ŠIMKOVÁ, Natalia GORODYLOVA, Petra ŠULCOVÁ

*Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Doubravice 41, 532 10 Pardubice, Czech Republic  
E-mail: Petra.Sulcova@upce.cz*

## INTRODUCTION

Corrosion is an undesirable phenomenon that causes deterioration of the material and the gradual reduction of its characteristics, or even complete destruction [1]. Corrosion represents considerable economic losses, estimated in the Czech Republic up to 25 billion Czech crowns per year. The corrosion costs include the losses connected with undertaking of measures against corrosion, reparation or even replacement of the equipment, and losses caused by reduction or cessation of production due to equipment damage. Therefore, development of new effective corrosion inhibitors is a very important research subject [2].

With respect to hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAP), it is an important technological material. One of its applications includes its use on metal implants as a coating which has two important functions: in one hand to protect the implant against corrosion, and in other hand, to improve implant's biocompatibility with the human body [3]. In view that HAP is suitable for the protection of the implants against corrosion due to its both structural and physical-chemical properties, it can be also functional in steel anticorrosion protection like do other phosphates [4]. Since this subject has not been studied before, it has become the main focus of this work.

The main goal of this study is to determine the possibility of doping of HAP with Mg, Zn and Al, to evaluate their influence on HAP properties, and to verify their application as corrosion inhibition pigment for steel.

## EXPERIMENTAL PART

In order to choose the appropriate synthesis conditions for the formation of doped HAP, thermodynamic stability of pure HAP phase in aqueous solution at RT was analysed and approved in laboratory conditions. Next, the selected precipitation conditions (Ca/P ratio; pH, precipitation speed) were adapted for the synthesis of doped HAP (Table 1, precipitation speed 2 ml/min). For the synthesis of the samples, 1M solutions of the starting compounds ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ ) were prepared. The exact concentration of these solutions was determined using analytical methods (titration, photometric and gravimetric analyses). The obtained precipitates were aged during 24 h, filtered and washed with distilled water to neutral pH, then dried at 80 °C for 6 h.

Analysis of the prepared samples was performed on an optical microscope (Dino - Lite Rack - MS 34 B) directly after precipitation and in 2 and 24 h of aging. Particle size measurement was performed before and after aging (Mastersizer 2000 MU, Mie approach). The phase composition of the dried samples was analysed on the benchtop X-ray diffraction instrument (Rigaku MiniFlex 600).

Table 1: Overview of the obtained samples and the synthesis conditions

Sample	Composition	(Ca+M)/P	pH	
1	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1	7	
1-Mg	$\text{Ca}_{9.5}\text{Mg}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
1-Zn	$\text{Ca}_{9.5}\text{Zn}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
1-Al	$\text{Ca}_{9.25}\text{Al}_{0.5}(\text{PO}_4)_6(\text{OH})_2$	0.975		
2	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67		
2-Mg	$\text{Ca}_{9.5}\text{Mg}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
2-Zn	$\text{Ca}_{9.5}\text{Zn}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
2-Al	$\text{Ca}_{9.25}\text{Al}_{0.5}(\text{PO}_4)_6(\text{OH})_2$	1.625		
3	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	3		
3-Mg	$\text{Ca}_{9.5}\text{Mg}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
3-Zn	$\text{Ca}_{9.5}\text{Zn}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
3-Al	$\text{Ca}_{9.25}\text{Al}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			2.96
5	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67		12
5-Mg	$\text{Ca}_{9.5}\text{Mg}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
5-Zn	$\text{Ca}_{9.5}\text{Zn}_{0.5}(\text{PO}_4)_6(\text{OH})_2$			
5-Al	$\text{Ca}_{9.25}\text{Al}_{0.5}(\text{PO}_4)_6(\text{OH})_2$		1.625	

At the next step, preliminary and accelerated corrosion tests of the samples were performed in order to verify their corrosion inhibition activity. Preliminary corrosion tests include the following: determination of pH and resistivity of aqueous suspensions of pigments (10%) during 28 days, gravimetric determination of weight loss of steel plates, and determination of corrosion indicators for the steel plates after being dipped into pigment extracts for 2 months and the change of pH and resistivity during this process. The formed corrosion products were analysed using optical microscope and their phase composition was determined by XRD analysis. Next, for accelerated corrosion tests, pigments were dispersed in water-based primer paint and applied on steel substrates (approx. 22 cm × 5 cm × 0.1 cm) and tested in corrosion testing chambers (periodic wet-dry exposure to 100% humidity with addition of 0.2 dm<sup>3</sup> of SO<sub>2</sub> gas at 38 °C (Hydrotherm 519, Erichsen Test Corrosion Chamber) during 3 weeks). Thickness of the dried paint coatings was controlled using a coating thickness gauge (Surfix easy I-FN, Phynix). The colour change of the paint samples during the corrosion tests was measured using spectrophotometer (ColorQuest XE). 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 analysed using optical microscope.

## RESULTS AND DISCUSSION

### Effect of doping on hydroxyapatite properties

According to optical microscopy results, the doped HAP formed as agglomerates of small crystallites of different size and shape similar to the pure HAP samples. Due to the very small percentage of the content of doped elements it was

assumed that the size and shape of crystallites of doped samples is similar to not modified HAP. In particular, under the chosen conditions, HAP phase forms as nanocrystalline which size and shape depends on the Ca/P ratio (with Ca/P = 1 form needle-like crystallites, with Ca/P = 1.67 - tubular plates, with Ca/P = 3 – needle-like, tubular plates and bulk crystallites), pH (with pH = 7 from larger and thinner crystallites, with pH = 12 - smaller and bulk crystallites), and 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  $\mu\text{m}$ . These values indicate the size of agglomerates, which are slightly larger than the values for not-doped HAP samples.

According to XRD analysis, most samples showed a single phase composition of HAP (hexagonal or monoclinic  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ). Only one sample - 1-Mg - consists of 2 phases: hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  and whitlockite  $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$  (Figure 1). Since 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 radii of these elements are approximately equal to or smaller than the radius of Ca ( $r(\text{Ca}^{2+}) = 1,06 \text{ \AA}$  (7),  $r(\text{Mg}^{2+}) = 0,89 \text{ \AA}$  (ca. 8),  $r(\text{Zn}^{2+}) = 0,9 \text{ \AA}$  (item 8),  $r(\text{Al}^{3+}) = 0,535 \text{ \AA}$  (item 6)).

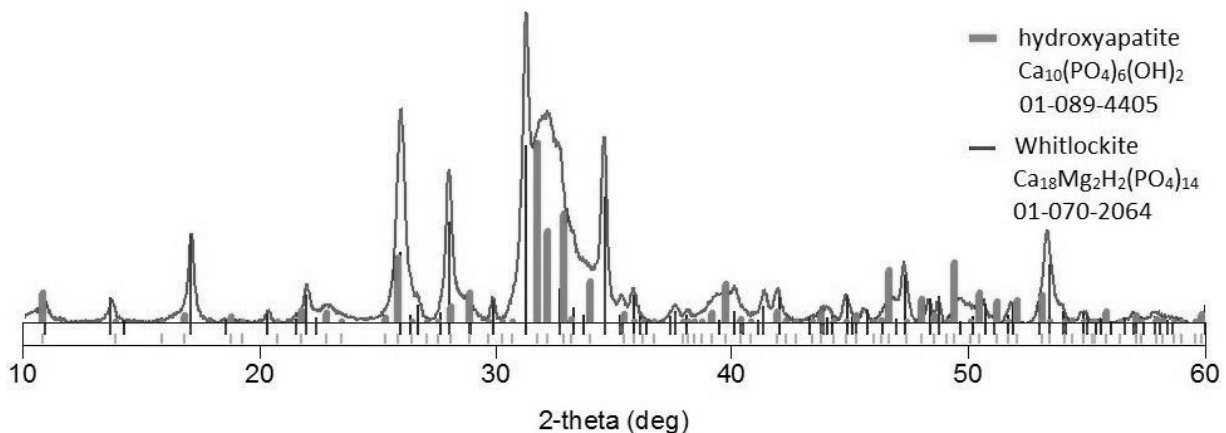


Figure 1: The diffraction pattern of the sample 1-Mg.

Based on the XRD patterns, i.e. XRD reflection width, crystallite size of the powders was also calculated. The size of the crystallites of doped HAP is in the range of 28,1-492  $\text{\AA}$  according to the results based on Scherrer equation, 53-71  $\text{\AA}$  - the Hall-Wagner method, and 59-106  $\text{\AA}$  - 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. In general, crystallites of doped samples are slightly smaller than for pure HAP. By comparison this result with the crystallite size observed on SEM images for pure HAP, it was found that the minimum values observed by SEM are comparable to the maximum values according to XRD analysis. It can be explained with the fact, that the bigger crystallites which are well observed at SEM images constitute only a minuscule part in relation to whole number of crystallites and therefore do not contribute much into diffraction line shape.

## Effect of doping on corrosion efficiency of hydroxyapatite

Measurement of pH and resistivity of aqueous suspensions of pigments is intended to stimulate the working conditions of the pigments. The pH in the range of 7-9 is considered optimal for the best corrosion inhibition, but in case of phosphate anticorrosion pigments, slightly acidic pH values are also acceptable. In turn, conductivity values indicate the concentration of dissociated species which are formed in result of the hydrolysis and may participate in the corrosion inhibition processes. Figure 2 shows change of pH and conductivity of the pigment suspensions during 28 days.

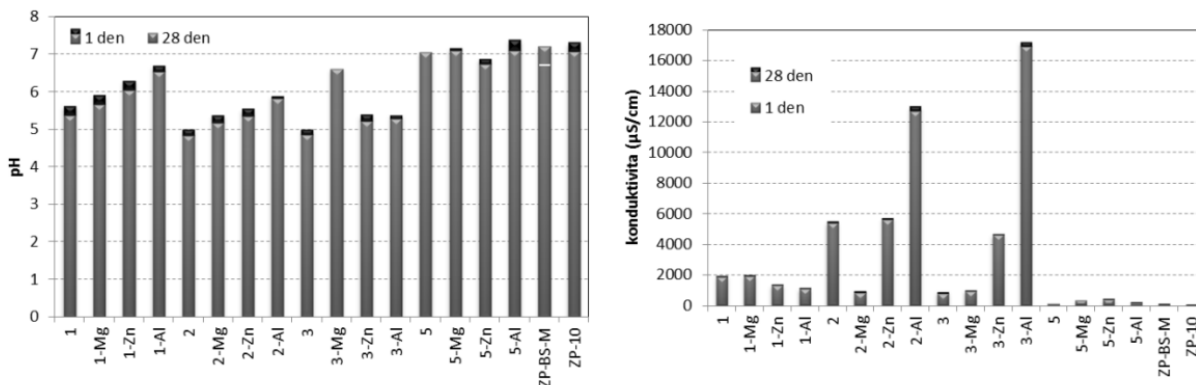


Figure 2: Results of preliminary corrosion tests: change of the pH and conductivity of the pigment suspensions during 28 days of aging.

The measured values show that in general, the hydrolysis of the pigment ions favours the formation of acid species, leading to reduction of pH. The conductivity of the samples was very different, but in general it increased indicating that the concentration of dissociated ions has increased over time.

The aqueous suspensions of the pigments were filtered and the pigments extracts were used for the evaluation of weight loss of steel plates, which were immersed in it during 2 months. During the test, there was observed a distinct colour change of the extracts due to release of corrosion products (rust). At the same time, the significant increase in pH also indicated intense corrosive processes (cathodic reaction leads to release of hydroxyl species:  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ). However, for all samples the conductivity value decreased. 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.

At the end of the test, corrosion indicators were calculated on basis of corrosion losses of steel plates. Figure 3 shows relative corrosive decrease for all tested samples. In this case, the water loss is a standard corresponding to 100%.

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

1. First group - pigments with high anticorrosive efficiency. Corrosion processes in the pigment extracts have been slowed down due to sufficient concentration of phosphates that inhibit corrosion processes (it is supported by the moderate conductivity values and the formation of Vivianite  $Fe_3(PO_4)_2 \cdot 8H_2O$  on steel surface). A sample of 1-Mg from this group showed the best anticorrosive properties, which may

be related to phase composition (Whitlockite phase may be more effective for corrosion protection than hydroxyapatite). This group comprises mainly of the samples of series 1 which are formed of crystallites of needle-like shape of the smallest size.

2. The second group - pigments of indifferent action towards corrosion processes. Concentration of phosphate in these extracts is insufficient for high anticorrosion efficiency (it is supported by a very low conductivity values and formation of  $\text{FeO}(\text{OH})$  as the main corrosion product). In general, this group includes the samples of series 5, extracts of which have similar to water properties towards corrosion.

3. The third group - pigments that promote corrosion processes. Here, the corrosion processes were very intensive due to intensive reaction between the pigment extracts and the steel plate (it is supported by the very high conductivity values, considerable surface damage and the formation of  $\text{FeO}(\text{OH})$  as the main corrosion product). Such behaviour can be explained by the presence of some hydrated complexes of calcium or doping elements, which act as catalysts of corrosion. In general, this group includes the samples of series 2 and 3.

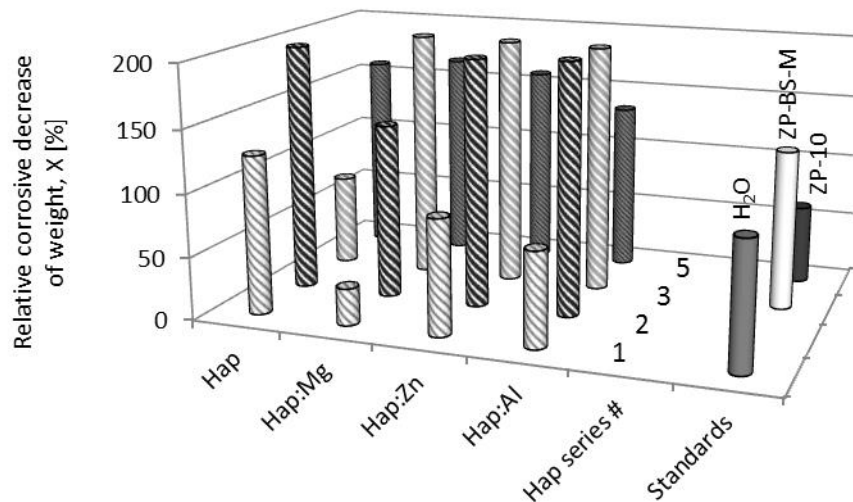


Figure 3: Results of the preliminary corrosion tests: relative decrease of weight of the samples (water - 100%).

For the accelerated corrosion tests, samples of 1, 1-Mg, 1-Zn, 2, 3, 5 and ZP-10 were selected. Examples of coating degradation for the selected samples are shown in Figure 4. The evaluation 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 where the most prominent cracks and corrosion spots were observed. The least damaged sample is the sample ZP-10 of commercial pigment. This result agrees well with the color change of the samples where for the most damaged sample was detected the highest colour difference. For all tested HAP samples, formation of small crystals on the coating surface was observed (Fig. 4). XRD analysis of these crystals identified only organic compounds in their phase composition, which indicates serious destruction of the coating. Thus,

based on the accelerated corrosion test, HAP samples showed poor corrosion properties for coating applications in comparison to standard pigment (ZP-10).

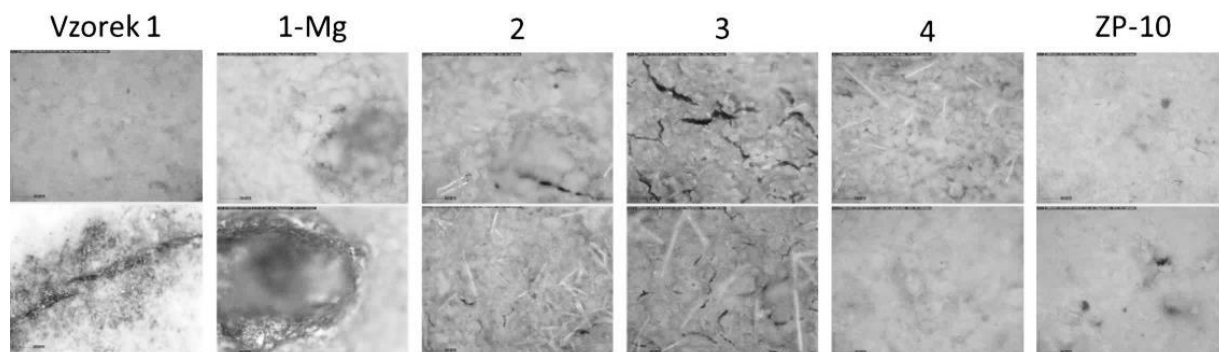


Figure 4: Appearance of coatings after accelerated corrosion test.

The poor corrosion properties of sample 3 in the accelerated corrosion tests agree well with the results of preliminary corrosion tests. For other samples, there is no consistency between the result of preliminary and accelerated corrosion tests.

## CONCLUSION

On basis of the obtained results it can be concluded that the employed synthesis conditions are suitable for the formation of crystalline HAP doped with Mg, Zn and Al. Only for one sample (1-Mg), two different phases (hydroxyapatite and whitlockite) were identified in the phase composition. Thus, 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 according to their anticorrosion effectivity: pigments with high corrosion inhibition efficiency; pigments of indifferent action towards corrosion processes; pigments that promote corrosion processes. It was also shown that the anti-corrosion efficiency of the prepared samples is related to the precipitation conditions. The best anticorrosion efficiency shows the samples of needle-like crystallites of smallest size (series 1). In addition, no doping effect can be observed except for the 1-Mg sample, which consists of two phases. Preliminary corrosion tests show that some samples of HAP have very high anticorrosive effectivity which in some cases is twice as high as effectivity of the commercial pigments.

On based of accelerated corrosion test, HAP samples showed 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.

## LITERATURE

- [1] Šustek S. Diplomová práce, Univerzita Pardubice, (2009).
- [2] Kalenda P, Veselý D, Antoš P. Univerzita Pardubice, Pardubice (2003).
- [3] Huang Y, Hao M, Nian X. *Ceramics Int.*, 42 (2016) 11876.
- [4] Gorodylova N, Dohnalová Ž, Šulcová P. et.al. *Prog Org Coat.* 93 (2016) 77.