***JAKUB MATUSIK***
*AGH – University of Science and Technology, Poland*

# SYNTHESIS AND CHARACTERIZATION OF Ca, Pb, Zn, Cu AND Cd CHLORAPATITES AND Pb-Cd CHLORAPATITES SOLID SOLUTIONS

The only minerals among divalent metal chlorapatites are: chloroapatite $Ca_5(PO_4)_3Cl$ and pyromorphite $Pb_5(PO_4)_3Cl$. To date, no occurrence of zinc, copper and cadmium chloroapatites have been noticed in hypergenic environment. Literature provides only scattered information about hydrothermally synthesized Zn and Cd chlorapatites. There is also no data on solid solutions of Pb and Cd in chlorapatites. The purpose of this research was aqueous synthesis of calcium, lead, zinc, copper and cadmium chlorapatites. Additionally, solid solutions of Pb- and Cd-apatites $(Pb_{5-x}Cd_x)(PO_4)_3Cl$ (x from 0 to 5) were prepared. Syntheses were prepared in aqueous solutions at normal conditions by mixing metal nitrates $Me(NO_3)_2$ (Me = Ca, Pb, Zn, Cu, Cd), potassium phosphate $KH_2PO_4$ and sodium chloride NaCl in proportions matching the stoichiometry of expected product. The precipitates were characterised by X-ray diffraction, infrared spectroscopy and scanning electron microscopy with EDS microanalyser. Partial substitution of $Pb^{2+}$ by $Cd^{2+}$ ions in the structure of pyromorphite was observed only in the range of $Pb_5(PO_4)_3Cl$ – $(Pb_4Cd_1)(PO_4)_3Cl$. However, instead of expected Zn, Cu and Cd chlorapatites, precipitation of hopeite $Zn_3(PO_4)_2{\cdot}4H_2O$, libethenite $Cu_2(PO_4)OH$, and cadmium phosphate $Cd_5H_2(PO_4)_4$ x $4H_2O$ was observed.

Единственными минералами среди двухвалентных металлических хлорапатитов являются хлорапатит $Ca_5(PO_4)_3Cl$ и пироморфит $Pb_5(PO_4)_3Cl$. До настоящего момента не обнаруживалось проявлений цинксодержащих, медьсодержащих и кадмийсодержащих хлорапатитов в гипергенных условиях. Литературные источники дают лишь разрозненную информацию о гидротермально синтезированных цинксодержащих и кадмийсодержащих хлорапатитах. Также отсутствуют сведения о твердых растворах Pb и Cd в хлорапатитах. Задачей настоящего исследования являлся синтез кальцийсодержащих, свинецсодержащих, цинксодержащих, медьсодержащих и кадмийсодержащих хлорапатитов из водных растворов. Были получены твердые растворы свинецсодержащих и кадмийсодержащих хлорапатитов $(Pb_{5-x}Cd_x)(PO_4)_3Cl$ (x от 0 до 5). Синтезированные вещества получены из водных растворов при нормальных условиях путем смешения нитратов металлов $Me(NO_3)_2$ (Me = Ca, Pb, Zn, Cu, Cd), фосфата калия $KH_2PO_4$ и хлористого натрия NaCl в пропорциях, соответствующих стехиометрическому составу ожидаемых продуктов. Выделившиеся фазы изучены с использованием методов рентгеновской дифракции, инфракрасной спектроскопии и растровой электронной микроскопии с микроанализом EDS. Частичное замещение ионов $Pb^{2+}$ ионами $Cd^{2+}$ в структуре пироморфита наблюдалось только в диапазоне $Pb_5(PO_4)_3Cl$ – $(Pb_4Cd_1)(PO_4)_3Cl$. Вместо ожидаемых цинксодержащих, медьсодержащих и кадмийсодержащих хлорапатитов наблюдалось выделение гопеита $Zn_3(PO_4)_2{\cdot}4H_2O$, либетенита $Cu_2(PO_4)OH$ и фосфата кадмия $Cd_5H_2(PO_4)_4$ x $4H_2O$.

## Introduction

Contamination of soils by heavy metals is undoubtedly one of the major issues of the modern soil science. Excessive levels of heavy metals can be hazardous to man, animals and plants. In situ formation of metal phosphates is a well established remediation technique described in the literature [1-3]. Because of relatively low solubility and high stability of phosphates over almost the entire pH and Eh range make them a perfect candidate for a waste solid form and the metal-bearing soil can be considered remediated after this treatment.

From all known metal chlorapatites present in nature, only calcium chloroapatite $Ca_5(PO_4)_3Cl$ and lead chloroapatite $Pb_5(PO_4)_3Cl$ (pyromorphite) have strictly defined structures and have been authorized by International Mineral Associacion (IMA). Literature provides information exclusively on zinc and cadmium

chlorapatites and their hydroxy forms, prepared by hydrothermal synthesis [4, 5]. There is also no information about solid solutions of Pb-Cd chlorapatites. Similar chemical properties (ionic radius, electronegativity, valency) of lead and cadmium, however, indicate possibility of their formation.

The purpose of this paper is: firstly to synthesise lead, calcium chlorapatites and to examine the applicability of the same conditions for precipitation of zinc and cooper chlorapatites, and secondly to prepare lead-cadmium solid solutions to state the maximal amount of cadmium that could be incorporated into pyromorphite structure. The results of this research will facilitate a distinct identification of selected heavy metal phosphates present in phosphate treated, metal-contaminated soils.

**Experimental methods**

***Chlorapatites synthesis***

All syntheses were conducted in aqueous media at normal conditions. A series of 300 ml volume solutions, containing metal cation (Me = Ca, Pb, Zn, Cu) or a mixture of metal cations ($Me = Pb_{5-x}Cd_x$, x = 0; 1; 2; 3; 4; 4,5; 4,75; 5) in the form of nitrates, potassium phosphate $KH_2PO_4$ and sodium chloride NaCl were prepared using analytical-reagent grade chemicals and deionized water, in equilibrium with the atmosphere. The solutions were added simultaneously to 1 liter of re-distilled water in a dropwise fashion (~5ml/min) using peristaltic pump, in proportions matching the stoichiometry of expected product. No attempt was made to alter pH. The solution with the forming phase was continuously stirred to provide homogenity. In all cases, the formation of the initial precipitate was noticed after ~10 minutes of the reaction and continued throughout the ~1 hour period of the experiment. In an attempt to improve crystallinity and increase crystal size of the synthesized phases, the aging of the precipitate was carried for 48 hours. The precipitates were then washed thoroughly and dried at 100 °C.

***Characterization methods***

Diffractograms of the samples were recorded using Philips APD PW 3020 X'Pert diffraction camera with Ni – filtered Cu – $K_\alpha$ radiation.

Infrared spectra were measured on a Bio-Rad FTS-60 spectrometer. Spectra were collected after 256 scans at 2 $cm^{-1}$ resolution in the region of 4000 – 400 $cm^{-1}$. Samples were prepared using the standard KBr pellets method.

The observations of the morphology and chemical analyses of the prepared samples were performed using HITACHI S – 4700 field emission scanning electron microscope coupled with EDS system. Prior to analyses samples were coated with gold.

**Results and discussion**

***Identification of* Ca, Pb, Zn, Cu *phosphates***

Chlorapatite $Ca_5(PO_4)_3Cl$ was the only phase formed in the reaction between calcium $Ca^{2+}$, phosphate $PO_4^{3-}$ and chloride $Cl^-$ ions detected by X–ray diffraction. IR spectra indicate presence of hydroxyl groups $OH^-$ in the structure of chlorapatite. In turn, the reaction of lead $Pb^{2+}$ with $PO_4^{3-}$ and $Cl^-$ ions leads to pyromorphite $Pb_5(PO_4)_3Cl$ formation as a sole product. Pyromorphite presence was confirmed by X-ray diffraction; narrow and sharp peaks of the diffractogram suggest good crystallinty of the synthesised phase. Well developed columnar crystals with characteristic hexagonal termination appear on the SEM microfotograph.

The precipitation of expected zincum $Zn_5(PO_4)_3Cl$ and cooper $Cu_5(PO_4)_3Cl$ chlorapatites was not observed. Instead hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ and libethenite $Cu_2(PO_4)OH$ formed respectively. Their presence is confirmed by XRD and chemical analyses. Broad peaks on the libethenite diffractogram indicate evident amorphous structure of this mineral in contrast to well crystallized hopeite whose diffractogram shows sharp peaks. Zincum and cooper chlorapatites are not likely to form at low temperatures, however it seems possible to synthesise those phases at moderately high temperatures [5].

All IR spectra except that of pyromorphite show a narrow peak at circa 1600 $cm^{-1}$. The presence of this band can be atributed to the presence of carbonates formed in the reaction with carbon dioxide from the atmosphere. The absence of carbonates on IR spectra of pyromorphite confirms its resistant, stable structure. A great number of bands on IR spectra of

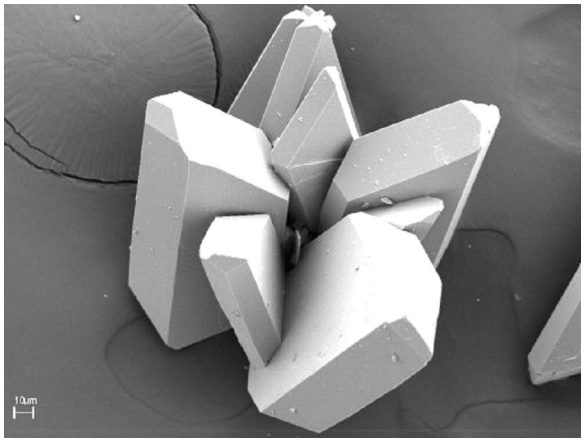


Fig.1 – SEM microfotograph of PCDTP

hopeite and libethenite in comparison with IR spectra of chlorapatite and pyromorphite may also indicate disturbed structure of those minerals (Table 1).

**Pb – Cd *chlorapatites series***

The complete substitution of $Pb^{2+}$ by $Cd^{2+}$ ions in the structure of pyromorphite synthesised according to the following equation: $(Pb_{5-x}Cd_x)(PO_4)_3Cl$ (x = 0; 1; 2; 3; 4; 4,5; 4,75; 5) was not achieved. The formation of continuous solid solution was observed only in the range: $Pb_5(PO_4)_3Cl$ – $(Pb_4Cd_{0,84})(PO_4)_3Cl$. In the reaction of phosphate $PO_4^{3-}$ and chloride $Cl^-$ with $Cd^{2+}$ ions the precipitation of cadmium phosphate phase of the formula $Cd_5H_2(PO_4)_4$ x $4H_2O$, described in the literature as PCDTP (pentacadmium dihydrogen tetrakis (phosphate) tetrahydrate)) was observed. PCDTP crystals belong to the monoclinic prismatic class on the contrary to hexagonal apatites. Well developed, large crystals of this phase are prestented on SEM microfotograph (Fig.1). The results of chemical analyses of the synthesised Pb–Cd phosphate series are given in Table 2. Low molar fraction of cadmium in the formed solid indicates that pyromorphite structure is resistant to substitutions of this element. The maximum amount of cadmium incorporated into pyromorphite structure (0,84 M) was achieved with the initial Pb:Cd ratio of 0,25:4,75.

**Table 1 – Frequency and assignments of the absorption bands in the IR spectra of samples**

| Molecular formula | $PO_4$ ($cm^{-1}$) | | | | $H_2O$, OH ($cm^{-1}$) | $CO_3^{2-}$ ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu$OH; $\delta H_2O$ | $\nu_4$ |
| $Pb_5(PO_4)_3Cl$ | 926 | 442 | 974<br>1032 | 542<br>573 | - | - |
| $Ca_5(PO_4)_3Cl$ | 964 | 476<br>976 | 1036<br>1105 | 567<br>605<br>638 | 3450 | 1665 |
| $Zn_3(PO_4)_2{\cdot}4H_2O$ | 972 | 434<br>478 | 1018<br>1055<br>1109 | 571<br>582<br>596<br>634 | 3216<br>2018 | 1657 |
| $Cu_2(PO_4)OH$ | 1167 | 428 | 985<br>1063 | 563<br>588<br>630 | 3414 | 1640 |

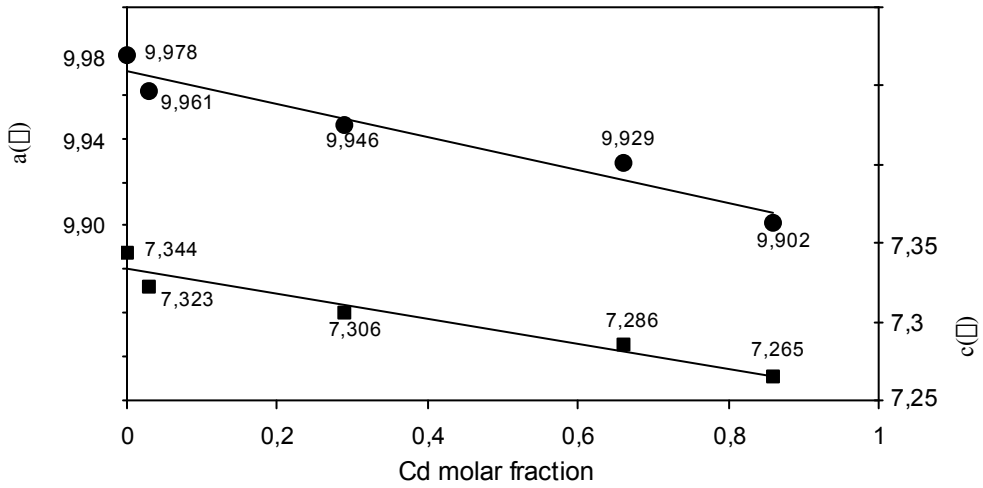



Fig.2 – Dependence of cell parameters versus amount of Cd in solid in the range from 0 – 0,84 M

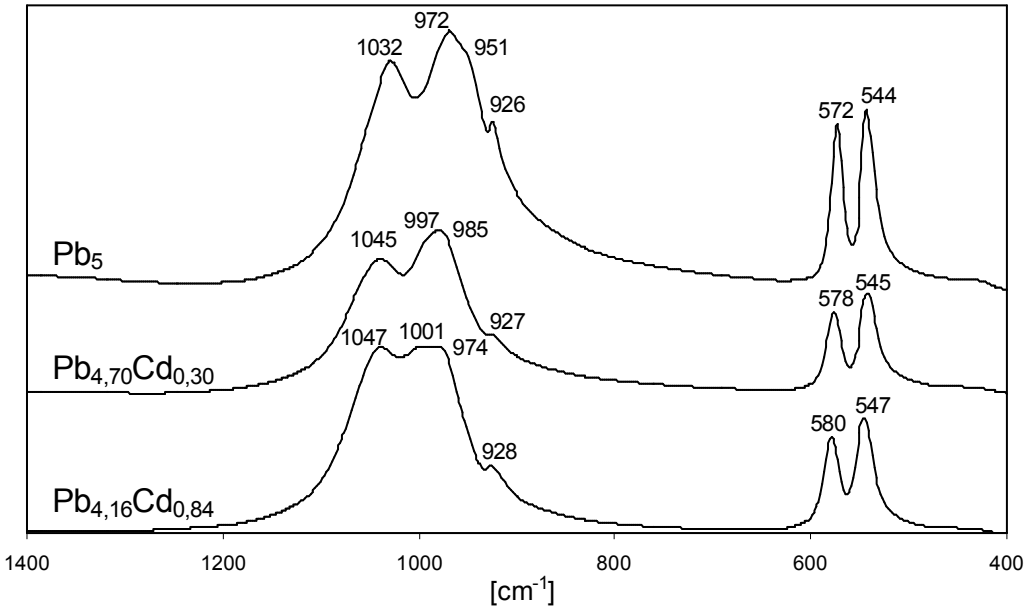



Fig.3 – Comparison of IR spectras of Pb – Cd phosphates series

**Table 2 – Chemical analyses of samples of solid solutions of lead – cadmium chlorapatites increased**

| Molecular formula of the expected product | Pb, Cd molar fraction in the formed solid |
|---|---|
| $Pb_5(PO_4)_3Cl$ | $Pb_5(PO_4)_3Cl$ |
| $(Pb_4Cd_1)(PO_4)_3Cl$ | $(Pb_{4,99}Cd_{0,01})(PO_4)_3Cl$ |
| $(Pb_3Cd_2)(PO_4)_3Cl$ | $(Pb_{4,97}Cd_{0,03})(PO_4)_3Cl$ |
| $(Pb_2Cd_3)(PO_4)_3Cl$ | $(Pb_{4,91}Cd_{0,09})(PO_4)_3Cl$ |
| $(Pb_1Cd_4)(PO_4)_3Cl$ | $(Pb_{4,70}Cd_{0,30})(PO_4)_3Cl$ |
| $(Pb_{0,5}Cd_{4,5})(PO_4)_3Cl$ | $(Pb_{4,34}Cd_{0,66})(PO_4)_3Cl$ |
| $(Pb_{0,25}Cd_{4,75})(PO_4)_3Cl$ | $(Pb_{4,16}Cd_{0,84})(PO_4)_3Cl$ |
| $Cd_5(PO_4)_3Cl$ | $Cd_5H_2(PO_4)_4 \times 4H_2O$ |

Diffractograms of the samples were used to calculate changes in their lattice parameters, owing due to the presence of cadmium in the solid. The analysis of the figure 2 indicate that the samples do not strictly obey Vegard's law. We noticed that the cell constants (a, c) decreased when the amount of cadmium in solid.

Characteristic absorption bands on IR spectras of Cd-substituted Pb-chlorapatites do not show major shifts in comparison with bands observed on pyromorphite spectra (Fig.3). A minor shift of bands towards higher wavenumber ($cm^{-1}$) values with the increase in the amount of cadmium in solid was observed.

**Acknowledgments**

The author would like to thank the following people for advice and assistance during the research: Daniel Wojnarski, Tomasz Bajda, Maciej Manecki, Adam Gaweł, Włodzimierz Mozgawa, Bartosz Budzyń and Olaf Borkiewicz.

**REFERENCES**

[1] *I. L. Shashkova, A. I. Rat'ko, N. V. Kitikova.* Colloids and surfaces A, (1999), 207-215.

[2] *J. Cotter-Howells, S. Caporn*. Applied Geochemistry 11, (1996), 335-342.

[3] *N. T. Basta, R. Gradwohl, K. L. Snethen, J. L. Schroder.* Journal of Environmental Quality 30, (2001), 1222-1230.

[4] *P. P. Mahapatra, D. S. Sarangi*. Indian Journal of Chemistry vol. 32A, (1993), 525-530.

[5] *E. R. Kreidler, F. A. Hummel*. The American Mineralogist vol. 55, (1970), 170-184.