

## STUDY OF BISHOFITE–PHOSPHATE ACID INTERACTION IN THE AQUEOUS SOLUTION

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By methods of pH monitoring of filtration solutions as well as due to determination of residual concentrations of ions  $Mg^{2+}$  and  $PO_4^{3-}$  the bishofite–phosphate acid interaction was studied with the given ratio  $[PO_4^{3-}]:[Mg^{2+}] = 0,187-5,24$ . The precipitation arising from the reaction was studied by chemical, thermal gravimetric and X-ray phase analysis and its compliance with the formula  $xNH_4MgPO_4 \cdot yMgHPO_4$  was established, where  $x = 0,25$ ;  $y = 0,75$ .

**Introduction.** Bishofite [1] which main compound is magnesium chloride is used as an accessible and natural raw material in order to get ammonium magnesium phosphates of various composition during fertilizer [2], antipyrine [3] production and other production.

It was also described in [4] how these complex fertilizers in the form of  $NH_4MgPO_4 \cdot xH_2O$  were got. The detailed analysis of range of publications was presented in [2], and in [5–7], where it was informed about various synthesis conditions of ammonium magnesium phosphates as well as results of their study by means of thermal gravimetric and X-ray phase analysis. The data received by various authors in these papers don't correspond to each other. This is particularly true for chemical

compounds, X-ray characteristics as well as for interpretation of thermal gravimetric data on the basis of which some authors say that  $NH_4MgPO_4$  is decomposed into  $NH_3$  and  $MgHPO_4$ , and other authors — into  $NH_3$ ,  $H_2O$  and  $Mg_2P_2O_7$  [2]; according to some researchers, this process is carried out because of composition of magnesium oxide and polyphosphates which compose  $Mg_2P_2O_7$  [7] at higher temperatures.

The known magnesium and ammonium phosphates were got by various authors mostly from laboratory reagents, the synthesis of these substances with the use of natural bishofite within a wide range of given  $[PO_4^{3-}]:[Mg^{2+}]$  ratios was not studied.

In the view of this, the purpose of this paper is to study the interaction between natural bishofite and phosphate acid, and

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also to specify the composition and nature of generated precipitations.

**Experimentation and discussion of results.** As basic substances for study the solution of natural bishofite from Poltava field was used which chemical composition was specified in analytical way [8], and which, being mined from the 2000 m depth, has selenium content hundred times bigger than the Earth crust has, phosphate acid and 25% ammonia solution (both reagents are A.R. purity).

A range of studies with the use of bishofite, ammonia and phosphate acid solution was prepared in the following way. The constant volume of bishofite solution (3 ml, at  $MgCl_2$  concentration 1,86 mol/l) in different series flasks was refilled with the variable volumes of phosphate acid at concentration 2,09 mol/l so that the given ratio  $[PO_4^{3-}]:[Mg^{2+}]$  ranges from 0,19 to 5,25. As a precipitation didn't emerge thereafter, each sample of transparent substance mixture solution was refilled with water up to the constant total volume and then by 7,8 ml 2,18 mol/l ammonia solution. Since then in most cases the precipitation emerged in samples and after the given ratio  $n = [PO_4^{3-}]:[Mg^{2+}] > 3,1$  the precipitation didn't emerge. After mixture settling during 14 days precipitations were filtered out and pH was measured in solutions (pH-150 MI), in order to calibrate pH-meter buffer solutions with pH = 1,68; 6,86 and 9,18 were used.

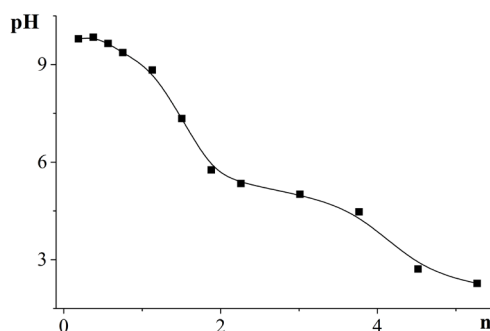
The thermal gravimetric analysis was conducted on derivatograph Q-1500-D of P. Paulik – L. Paulik – L. Erdey system, samples tipped the scale of  $0,2 \cdot 10^{-3}$  kg and were located in platinum and corundum crucibles, heating rate - 0,167 deg/s; DTA – 250; DTG – 500.

X-ray phase analysis (XRPA) was carried out on DRON-3M with the copper radiation and computer registration of X-ray patterns, the determination error  $2\theta$  was  $\pm 0,04^\circ$ .

Magnesium and phosphate ion concentration in filtrates were specified by methods [9].

The dependence of pH of filtration solutions of one of the cross section  $MgCl_2$  system (of bishofite) –  $NH_3 \cdot H_2O - H_3PO_4 - H_2O$  on the given ratio  $n = [PO_4^{3-}]:[Mg^{2+}]$  was shown in the fig. 1. In this case two bends are observed: the first by  $n = 0,75-2,0$  and  $pH = 5,5-9,5$ , and the second by  $n = 3,0-4,5$  and  $pH = 2,5-5,0$ . Both bends are situated in wide ranges not only basic ratios but also pH which is evidence of complex nature of interaction and a possibility to compose not individual substances but mixtures or solid solutions of variable composition. For instance, the composition of  $Mg_5(OH)(PO_4)^3 \cdot xH_2O$  [10],  $NH_4MgPO_4 \cdot H_2O$  [4],  $MgHPO_4 \cdot 3H_2O$  [2] and  $Mg(H_2PO_4)_2 \cdot zH_2O$  [11] is possible in exploratory conditions. At high pH values  $\sim 9,5$  magnesium hydroxyapatite of low solubility, at pH  $\sim 9,0$  and less in the alkaline area – ammonium magnesium phosphate, at pH  $\sim 4,7 - 6,0$  – magnesium hydrogen phosphate [2], at pH less than 4,5 – magnesium dihydrogen phosphate can be composed.

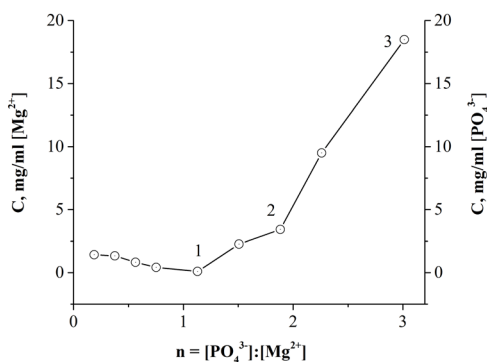
Besides these compounds, very soluble in water ammonium hydrogen phosphate and



**Fig. 1. The dependence of pH of filtration solutions of one of the cross section  $MgCl_2$  system (of bishofite) –  $NH_3 \cdot H_2O - H_3PO_4 - H_2O$  on the given ratio  $n = [PO_4^{3-}]:[Mg^{2+}]$**

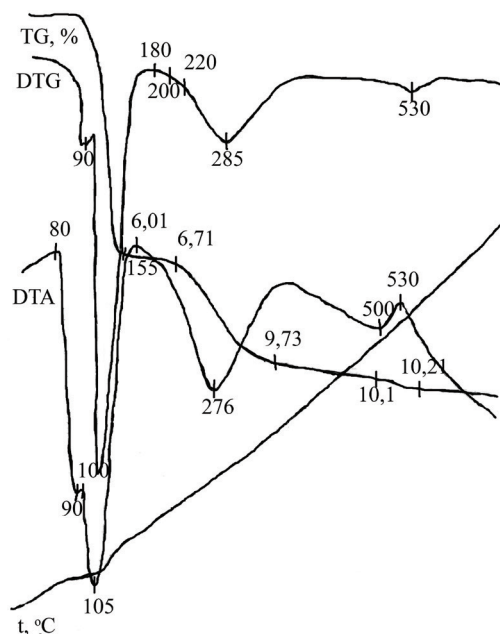
ammonium dihydrogen phosphate are composed in the system at basic  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] > 3,1$ . This set of various products in the explored system is explained by course of concurrent ion hydrolysis exchange reactions involving ions of weak bases  $\text{Mg}(\text{OH})_2$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as well as phosphate ion.

The determination of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ion concentration in filtration solutions is shown in the fig. 2. The first fracture at basic  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 1$  shows that  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  go almost completely into precipitation in these conditions, while at  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 2$  the  $\text{PO}_4^{3-}$  concentration in the solution starts its heavy increase, and at given  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] > 3,1$  the precipitation doesn't emerge anymore because of acid ammonium phosphate composition. As neither pH measurement method nor residual concentration solubility method doesn't explain chemical nature of precipitations, because the selected research object is a cross section of multicomponent heterogenic system, separate precipitation syntheses at given ratios  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 1:1$  and  $2:1$  were carried out. Emerged precipitations were studied by means of chemical, thermal gravimetric and X-ray phase analysis.



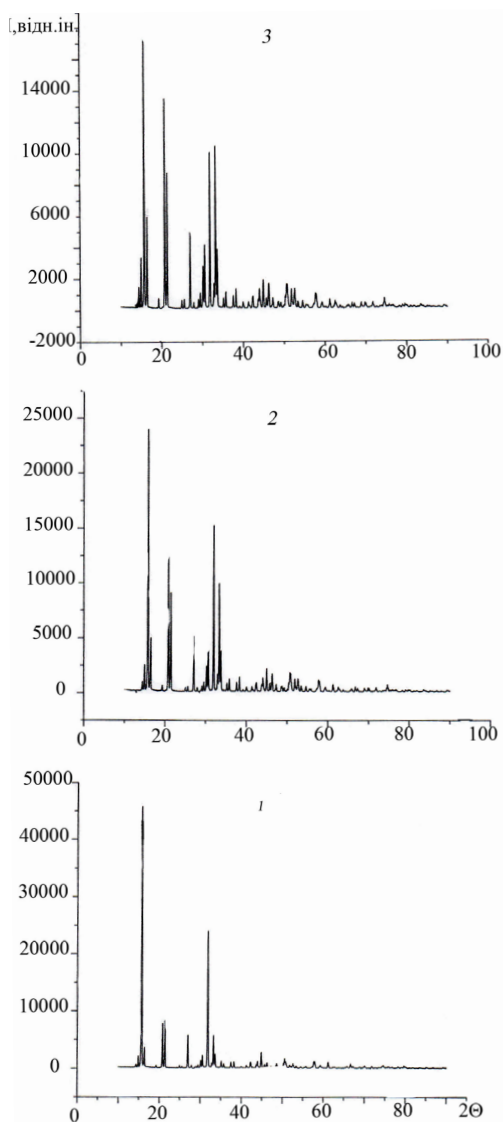
**Fig. 2. Dependence of residual concentrations** in filtration solutions of one of the cross section  $\text{MgCl}_2$  system (of bishofite) –  $\text{NH}_3 \cdot \text{H}_2\text{O} - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$  on the given ratio  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}]$

In the fig. 3 the thermogram of precipitation got at given ratio  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 1:1$  is shown, which is similar in nature of thermal effects and their temperature values to the thermogram of precipitation got at  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 2:1$ ; it is noticeable due to DTA and TG curves that the loss of mass starts from  $80^\circ\text{C}$ , which corresponds to two deep endo-effects imposed on each other; their presence is explained by ammonia and water release [2], minimal endo-effect at  $276^\circ\text{C}$  is connected with the thermolysis of  $\text{MgHPO}_4 \cdot x\text{H}_2\text{O}$  which this substance has [5]; as to the loss of mass at  $500\text{--}530^\circ\text{C}$  (exo-effect), according to data [2] ammonia residua release. There is one more explanation excerpt for this one – at temperatures above  $500^\circ\text{C}$  the hydroxyl substance group of thermal hydrolysis impurities or products can eliminate, for example, magnesium hydroxyapatite  $\text{Mg}_5(\text{OH})(\text{PO}_4)$  which content is  $\sim 3\text{--}4\%$ . The exo-effect at  $500\text{--}530^\circ\text{C}$  is caused by



**Fig. 3. The thermogram of precipitation got** at given ratio  $n = [\text{PO}_4^{3-}]:[\text{Mg}^{2+}] = 1:1$

phase transition formed due to the thermolysis of  $Mg_2P_2O_7$ . If we compare results of thermal gravimetric analysis with data [2], we'll see that precipitations got in this paper give the same thermal effects specified both for  $NH_4MgPO_4 \cdot H_2O$  and for  $MgHPO_4 \cdot 3H_2O$ .



**Fig. 4.** X-ray patterns  $NH_4MgPO_4$  (1) and precipitations got at given ratio  $n = [PO_4^{3-}]:[Mg^{2+}] = 1:1$  (2) and  $2:1$  (3)

In order to study the nature of got precipitations they were studied by means of X-ray phase analysis (fig. 4), for comparison the weight form  $NH_4MgPO_4 \cdot H_2O$  got in analytical conditions was used. As is shown in the fig. 4, all three X-ray patterns are of the same type, have the same values of angles of reflection within the study error but differ in intensities of separate lines. At that, the intensity of these lines increases downwards given  $n = [PO_4^{3-}]:[Mg^{2+}]$  and upwards pH up to 9,0–9,5. This is only possible if precipitations got at given  $n = [PO_4^{3-}]:[Mg^{2+}] = 1:1$  and  $2:1$  are phases of variable composition, for example,  $xNH_4MgPO_4 \cdot yMgHPO_4 \cdot zH_2O$ . The found loss of mass 10,29 % corresponds to composition at  $x = 0,25; y = 0,75; z = 0$ .

In order to specify nature of emerged precipitations completely the number of magnesium and phosphorus contained in them as well as loss of mass when frying up to 600 °C were determined, found  $\Delta m = 10,30$  mass %.

The data of chemical precipitation analysis indicate sedimentation which found a ratio  $n = [PO_4^{3-}]:[Mg^{2+}] = 1:1$ , as an given ratio  $n = [PO_4^{3-}]:[Mg^{2+}] = 1:1$ , and an given ratio  $n = [PO_4^{3-}]:[Mg^{2+}] = 2:1$ . That is, it corresponds to formula  $0,25NH_4MgPO_4 \cdot 0,75MgHPO_4$ . Exactly from this perspective the differences in interpretation of these studies of  $NH_4MgPO_4 \cdot H_2O$  by various authors [2] and [5] by means of the same methods can be explained.

### Conclusion

When nature bishofite solution interacts with phosphate acid in the ammonia medium within the range of given ratios  $n = [PO_4^{3-}]:[Mg^{2+}] = 1-2$  and at pH filtrates 5,5–9,5, the phase of variable composition  $0,25NH_4MgPO_4 \cdot 0,75MgHPO_4$  which can be used during the fertilizer production is formed in the precipitation.



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## АНОТАЦІЯ

*Перепелиця О.П., Петренко Т.В., Самчук А.І., Хоменко Б.С. Дослідження взаємодії бішофіту з фосфатною кислотою у водному розчині // Біоресурси і природокористування. – 2016. – 8, №3–4. – С. 35–39.*

*Методами рН-метрії фільтраційних розчинів, визначення залишкових концентрацій іонів  $Mg^{2+}$  і  $PO_4^{3-}$  досліджено взаємодію розчину бішофіту з фосфатною кислотою при заданому співвідношенні  $[PO_4^{3-}]:[Mg^{2+}] = 0,187-5,24$ . Осад, який утворюється внаслідок реакції, досліджено методами хімічного, термогравиметричного та рентгенофазового аналізу. Встановлено його відповідність формулі  $xNH_4MgPO_4 \cdot yMgHPO_4$ , де  $x = 0,25$ ;  $y = 0,75$ .*

## АННОТАЦИЯ

*Перепелица О.П., Петренко Т.В., Самчук А.И., Хоменко Б.С. Исследование взаимодействия бишофита с фосфатной кислотой в водном растворе // Биоресурсы и природопользование. – 2016. – 8, №3–4. – С. 35–39.*

*Методами рН-метрии фильтрационных растворов, определения остаточных концентраций ионов  $Mg^{2+}$  и  $PO_4^{3-}$  исследовано взаимодействие раствора бишофита с фосфатной кислотой при заданном соотношении  $[PO_4^{3-}]:[Mg^{2+}] = 0,187-5,24$ . Осадок, который образуется в результате реакции, исследован методами химического, термогравиметрического и рентгенофазового анализов. Установлено его соответствие формуле  $xNH_4MgPO_4 \cdot yMgHPO_4$ , где  $x = 0,25$ ;  $y = 0,75$ .*