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# ACTIVITY OF PHOSPHORUS OF SYNTHETIC Fe-K-P COMPOUNDS IN SUPERPHOSPHATE FERTILIZERS AS AFFECTED BY pH AND IONIC STRENGTH<sup>(1)</sup>

Luís Ignácio Prochnow<sup>(2)</sup>, Gustavo Marques Biasioli<sup>(2)</sup>, Arnaldo Antonio Rodella<sup>(2)</sup>, Sérgio Luís de Jesus<sup>(2,3)</sup>, Célia Regina Montes<sup>(2,3)</sup> & Luís Reynaldo Ferracciú Alleoni<sup>(2)</sup>

## SUMMARY

The concentration of orthophosphate ions released from Fe-K-P compounds ( $\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$ ) present in superphosphates increases with pH, which initially suggests that the agronomic effectiveness of P fertilizers containing high amounts of these compounds would also increase with soil pH but studies considering activity, instead of concentration, are necessary. With this purpose, both compounds were synthesized under laboratory conditions, characterized by elemental chemical analysis, optical microscopy, X ray diffractometry, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), and used in a solubility study. Solutions of 0.01, 0.05 and 0.1 mol L<sup>-1</sup> NaCl with pH adjusted to 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5 were prepared for the solubility study of H8-syn, H14-syn and a phosphate rock (PR) from Brazil. The orthophosphate activity as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  was calculated in each situation as related to pH and ionic strength using software MINTEQ. The remaining precipitates after equilibrium were chemically analyzed and subjected to X ray, SEM and EDS. Results of chemical analysis and instrumental techniques confirmed the preparation method. The activity of orthophosphate ions of both compounds tended to decrease under increasing pH and/or ionic strength of the solution, which in turn suggests that an increase in the solution pH does not necessarily promote an increase in the P bioavailability for plant uptake. This can be important when evaluating agronomic data of P fertilizers with high contents of these two Fe-K-P compounds.

**Index terms:** Phosphate fertilizers, cationic impurities, phosphorus activity, phosphorus bioavailability.

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**RESUMO:** *EFEITO DO pH E DA FORÇA IÔNICA NA ATIVIDADE DE FÓSFORO ORIUNDO DE COMPOSTOS SINTÉTICOS DO TIPO Fe-K-P DE SUPERFOSFATOS*

*O aumento do pH da concentração de íons ortofosfatos liberados de compostos do tipo Fe-K-P ( $\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$  e  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$ ), presentes em superfosfatos, evidenciam, inicialmente, que a eficiência agronômica de fertilizantes fosfatados, com elevadas quantidades destes, poderiam aumentar com o pH do solo; todavia, estudos que considerem atividades, em vez de concentração, são necessários. Com este propósito, ambos os compostos foram preparados em condições de laboratório (H8-sin e H14-sin), caracterizados por análise química elementar, microscopia óptica, raios X, microscopia eletrônica de varredura (MEV) e espectrometria de energia dispersiva (EDS), e utilizados em um estudo de solubilidade. Soluções de NaCl, nas concentrações de 0,01, 0,05 e 0,1 mol L<sup>-1</sup> com o pH ajustado de 3 a 7,5, foram utilizadas no estudo de solubilidade envolvendo o H8-sin, H14-sin e um fosfato de rocha apatítico do Brasil. O programa MINTEQ foi utilizado para calcular a atividade dos ortofosfatos  $\text{H}_2\text{PO}_4^-$  e  $\text{HPO}_4^{2-}$  em cada situação de pH e força iônica. O tipo de precipitado remanescente, quando atingido o equilíbrio, foi submetido à análise química elementar, raios X, MEV e EDS. As análises confirmaram que os métodos de preparo foram adequados para ambos os compostos. A atividade dos íons ortofosfatos oriundos da reação de hidrólise do H8-sin e H14-sin tendeu a diminuir com o aumento do pH e, ou, a força iônica da solução, o que mostra que um aumento da concentração em solução não necessariamente significa um aumento da biodisponibilidade de P às plantas. Estes dados poderão ser importantes para compreender a eficiência de fertilizantes fosfatados que contêm elevadas quantidades desses compostos.*

*Termos de indexação:* fertilizantes fosfatados, impurezas catiônicas, atividade de fósforo, biodisponibilidade de fósforo.

## INTRODUCTION

As anticipated by Catchcart (1980), levels of water-insoluble compounds are on the rise in acidulated phosphate fertilizers (APF) as the industry is being forced to use lower-grade phosphate rock (PR). For many phosphate rocks (PR), high amounts of contaminants or even some apatite bounded to contaminants are presently being discarded to adequate the apatite concentrates to the standards set by the legislation of several countries by producing high water-soluble APF (Brazil, 1982; Official Journal of the European Communities, 1975).

In superphosphates, two of the most common water-insoluble compounds are  $\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$  (H8) and  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$  (H14) (Lehr et al., 1967; Frazier et al., 1991; Prochnow et al., 2003b). H8 preferentially forms at  $\text{P}_2\text{O}_5$  concentrations below 39 % and H14 forms at  $\text{P}_2\text{O}_5$  concentrations in the range of 39 to 70 % (Frazier et al., 1989). As a consequence, H8 and H14 generally occur in single and triple superphosphates, respectively.

Some studies were carried out on the agronomic effectiveness of APF with lower water solubility, due to the presence of compounds of the Fe-Al-P type and compared to those specified by legislation (high in water solubility and almost free of Fe-Al-P compounds). Many greenhouse and some field studies suggest that the level of impurities in APF would have to be increased above current levels before effectiveness

would be affected (Mullins & Sikora, 1992, 1995; Sikora et al., 1989; Prochnow et al., 2003a, 2003b). Better use of low-grade PR is possible by producing agronomically effective APF varying in water solubility (Lehr, 1980).

Prochnow et al. (2003a) showed that more P, as measured in terms of orthophosphate concentration in solution (Murphy & Riley, 1962), was released from both compounds as pH increased in the 0.01 M KCl solution (pH 3.0–7.5) and that more P was released from H14 than H8, both synthesized at laboratory conditions (49 % of the total P at pH 6.0 was released from H14 versus only 11 % from H8). The authors initially suggest that the agronomic effectiveness of P fertilizers containing high amounts of H8 and/or H14 would increase as soil pH increases, but further studies considering activity, which could represent the bioavailability of chemical species to plants more adequately, are required. In the soil system, the great majority of ions are free or interacting with other ions and molecules, thus forming ion pairs (Sposito, 1994). Around 100 to 200 soluble complexes can be found (Sposito, 1984) and activity is important to understand the bioavailability of chemical elements to plants. As an example, Pavan & Bingham (1982) showed that activity was closer related to Al bioavailability to coffee seedlings than its concentration. Likewise, orthophosphate activity in solution could represent bioavailability better than the concentration. This information would be relevant with a view to gain insights on agronomic data of APF with high H8 and,

or, H14 contents in different conditions of soil solution. This study aimed to gather information regarding this issue.

## MATERIAL AND METHODS

The H8 and H14 compounds were synthesized based on information provided by Lehr et al. (1967) and Frazier et al. (1991) and were identified as H8-syn and H-14 syn, respectively. During the synthesis process, the crystal morphology (hexagonal rods and pseudohexagonal plates for H8-syn and H14-syn, respectively) was monitored by optical microscopy, using a Carl Zeiss Model Axioskop polarizing light microscope. The yield was 206 and 80 g of H8-syn and H14-syn, respectively. Both compounds were characterized by elemental chemical analysis, optical microscopy, X ray diffractometry, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Samples of the two compounds were analyzed for free water, water of hydration and total P, Fe, K, S-SO<sub>4</sub> and soluble P contents in neutral ammonium citrate (NAC). The analytical procedure for total P, Fe and K involved the digestion of a 1.00 g sample, using a mixture of concentrated HClO<sub>4</sub>.HNO<sub>3</sub> at 2:1 volume ratio, followed by filtration through Whatman N° 42 filter paper. The filtrate was collected in a 500 mL volumetric flask and diluted to volume with distilled water. The total P concentration was determined by the molybdovanadophosphate procedure [Association of Official Analytical Chemists (AOAC), 1999]. The Fe concentration was determined using a Perkin-Elmer Model 560 atomic absorption spectrophotometer, and K using a Corning Model 400 flame spectrometer. The AOAC procedure (1999) was used to determine S-SO<sub>4</sub> and soluble P in NAC and in water. The free water was determined by the vacuum desiccation method (AOAC, 1999). After removing the free water, the water of hydration was determined by distillation, according to the n-amyl alcohol method (Duncan & Brabson, 1969). Total water was obtained by the summation of free water and water of hydration.

The two Fe-K-P compounds in the mother liquor, after being washed with water and dried with acetone, were examined using the Carl Zeiss Model Axioskop polarizing light microscope, to obtain the morphological and optical data, including crystal system, habit, and refractive indices. Refractive indices were measured by the Becke line method (Wahlstrom, 1979) with certified refractive index oils.

Samples of 20 g of H8-syn and H14-syn were prepared for X ray analysis by grinding with 10 mL Freon for 7 min in an impact grinder. The samples were step-scanned with a Philips Model X'Pert PW 3710 X ray powder diffractometer from 3.0 to 70.0 degrees 2-Theta, at a step size of 0.04 degree 2-Theta and a dwell-time of three seconds, with Cu

radiation produced at a power setting of 40 kV and 40 mA. The data were analyzed using the powder diffraction file (PDF) database [International Center for Diffraction Data (ICDD), 1999], to which XRD patterns for Fe-Al-P compounds were added, as described by Frazier et al. (1991).

A portion of H8-syn and H14-syn was placed on individual sample stubs using double-faced scotch tape coated with carbon. The samples were scanned in a Jeol Model JSM 5600LV SEM with accelerating voltage from 15 to 30 kV using a Noran/Voyager EDS operating in a range of 0 to 10 kV. The scanning procedure targeted structures with defined micro-morphology in the sample.

Solutions of 0.01, 0.05 and 0.1 mol L<sup>-1</sup> NaCl with pH adjusted to 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5 were used in the solubility study of H8-syn, H14-syn and a Catalão PR (13 % P<sub>2</sub>O<sub>5</sub>) from Brazil containing, besides the apatite, silicate and oxide minerals. The solutions were chosen based on the concentrations and pH of regular agricultural soils. A 50 mL volume of each of these solutions was added to a plastic snap cap vial in which a 166 mg sample of each P source was also added. The samples were shaken continuously until the solution pH reached the equilibrium near the target pH values. The pH was adjusted to the target pH every 24 h by adding drops of 0.01, 0.1 or 1.0 mol L<sup>-1</sup> solution of either KOH or HCl.

After reaching the equilibrium, the samples were filtered through Whatman N° 42 filter paper, and the P, Fe, K, S-SO<sub>4</sub>, Na and Cl concentration was measured in the Murphy and Riley (1962) solution, by atomic absorption, flame spectroscopy, by the gravimetric method of barium sulfate (AOAC, 1999), flame spectroscopy, and titration with AgNO<sub>3</sub> [Laboratório nacional de referência vegetal (LANARV), 1983], respectively. Phosphorus released from each P source was expressed as the percentage of the added P amounts. MINTEQA (Allison et al., 1991) was used to calculate the separate activity of the orthophosphates H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> in each situation, as related to pH and ionic strength. The activities of both orthophosphate species were summed up and used in discussions once both forms are bioavailable to plants.

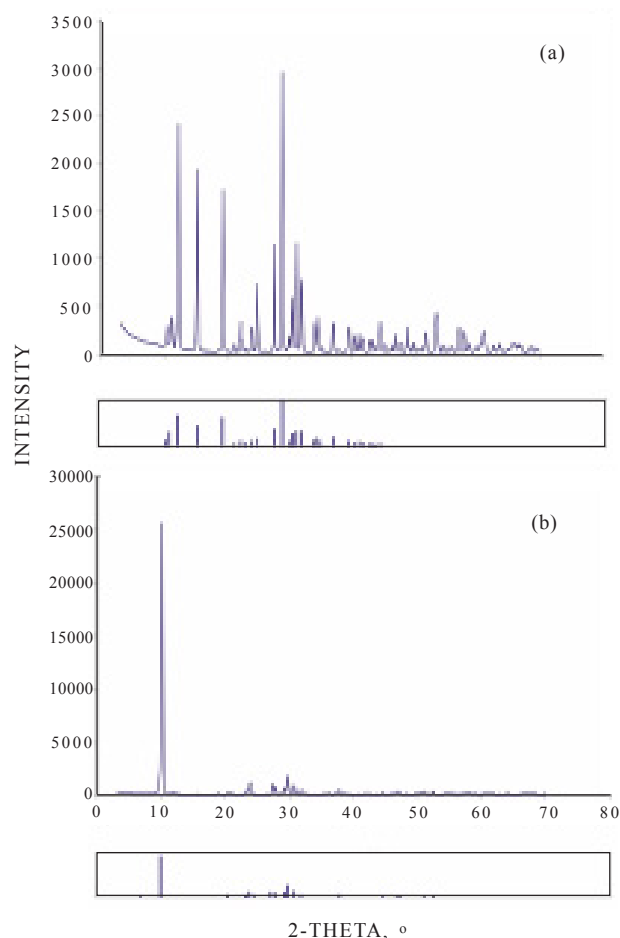
To gather information on the type of remaining precipitates in the filter paper, a larger batch (4.98 g of the compound in 1.5 L) of both compounds was prepared with equilibrium solutions reaching, approximately, pH 5.0 and 7.0. The remaining precipitates in the filter paper were chemically analyzed and submitted to X ray, MEV and EDS, as described above.

## RESULTS AND DISCUSSION

Concentration of total P, Fe, K and water of hydration of H8-syn and H14-syn (Table 1) were very

close to those expected for H8 and H14, considering the chemical composition of their empirical formula. The amounts of S-SO<sub>4</sub> in H8-syn (1.0 %) and H14-syn (0.1 %) were accounted as remaining Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O (one of the initial reagents) in the materials. The high available P (NAC + H<sub>2</sub>O), as related to the total content of P (99 and 97 % for H8-syn and H14-syn, respectively) is mainly due to the solubility in NAC, not in water. This high solubility in NAC does not necessarily mean a high P bioavailability for plant uptake. As explained by Prochnow et al. (2003a), two factors interact when high P amounts are extracted by NAC from compounds of the Fe-P type: (1) citrate is a chelating ligand that can complex Fe with a high formation constant (higher than Ca-P or Al-P), and (2) Fe-P minerals are more soluble in high pH solutions. Therefore, the amounts extracted by NAC can be higher than the amounts actually bioavailable for plant uptake.

The optical data of both compounds were found to be essentially homogeneous and identical to H8 (hexagonal rods; uniaxial (+);  $\omega = 1.595$ ,  $\epsilon = 1.601$ ) and H14 (orthorhombic-hexagonal shaped plates; biaxial (-);  $\alpha = 1.556$ ,  $\beta = 1.600$ ,  $\gamma = 1.606$ ). In terms of peak location and intensity the X ray powder diffraction patterns obtained for the H8-syn and H14-syn samples agreed very well with the X ray patterns for these compounds taken from the Powder Diffraction File (PDF) (ICDD, 1999) or with those cited by Frazier et al. (1991) (Figure 1). The SEM photomicrographs of specific areas of crystals in the H8-syn and H14-syn samples are shown in Figure 2. The morphology of the compounds which identified hexagonal rod crystals for H8-syn and pseudo-hexagonal plates for H14-syn was in line with the morphology suggested by Frazier et al. (1989). Our EDS analysis of specific



**Figure 1. X ray diffractogram and powder diffraction file (PDF) data of the compounds H8-syn (A) and H14-syn (B).**

**Table 1. Elemental chemical composition – theoretical and obtained by analytical methods – for the compounds H8 and H14**

Determination	H8		H14	
	Theoretical	Analytical	Theoretical	Analytical
%				
Total P	20.8	20.0	23.6	23.3
NAC Soluble P	-	19.8	-	21.8
Water Soluble P (WSP)	-	0.03	-	0.8
Available P (NAC + H <sub>2</sub> O)	-	19.8	-	22.6
(WSP/Available P) * 100	-	0.2	-	3.5
Fe	18.8	17.4	16.0	14.3
K	4.3	4.7	3.7	3.9
S-SO <sub>4</sub>	-	1.0	-	0.1
Free water	-	0.3	-	0.1
Water of Hydration	12.1	11.9	6.8	7.3
Total water	-	12.2	-	7.4



areas of both crystals suggests that the compounds consisted basically of Fe, K and P (data not shown). No other morphological structures were found in the samples of H8-syn and H14-syn. Results of chemical analysis (Table 1), optical microscopy, X ray diffractometry (Figure 1), compound morphology (Figure 2), and EDS analysis of areas of the crystals confirmed that the method of preparation was successful and that H8-syn and H14-syn can be considered as  $\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$ , respectively, with no contaminants.

Figure 3 shows the amount of P released by the P materials as a function of the pH at equilibrium of the 0.01 mol L<sup>-1</sup> NaCl solution. Similar trends were observed for the other two solutions, i.e., 0.05 and 0.1 mol L<sup>-1</sup> NaCl. The amounts of released P when Catalão PR was used tended to decrease with increasing pH. This is consistent with solubility studies on other PR sources and agronomic evaluation of apatitic PR (Engelstad et al., 1974; Chien et al., 1975). For the Fe-P compounds the trend was opposite (Figures 3 and 4), with a slight increase in the amounts of P released with increasing pH. Also, the amount of P released from H14-syn was much higher

than from H8-syn. Similar results were observed by Prochnow et al. (2003a), who suggested that H14 would be a more effective P source for plants than H8 and that both Fe-K-P compounds could be agronomically more effective in high pH soils.

For H8-syn there was a clear trend towards a higher P release when using 0.01 mol L<sup>-1</sup> NaCl, compared to the other two NaCl concentrations (Figure 4). This should be related to higher hydrolysis of this compound at lower ionic strength. The same trend was not observed for the other two P materials, most likely due to the higher amounts of P released.

The activity of  $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  followed some of the trends discussed for concentration, i.e., (1) decrease in activity with increasing pH for Catalão PR and (2) a much higher activity when using H14-syn, compared to H8-syn and PR (data not shown). For H14-syn, the effect of ionic strength was evident for activity at pH > 4, as shown in figure 5 (activity above pH 4: 0.01 > 0.05 > 0.1 mol L<sup>-1</sup> of NaCl). For the NaCl solutions of 0.05 and 0.1 mol L<sup>-1</sup> the activity tended to increase up to around pH 5 and decrease afterwards. For the NaCl 0.01 mol L<sup>-1</sup>, the trend was the same with a flex point at around pH 6. The

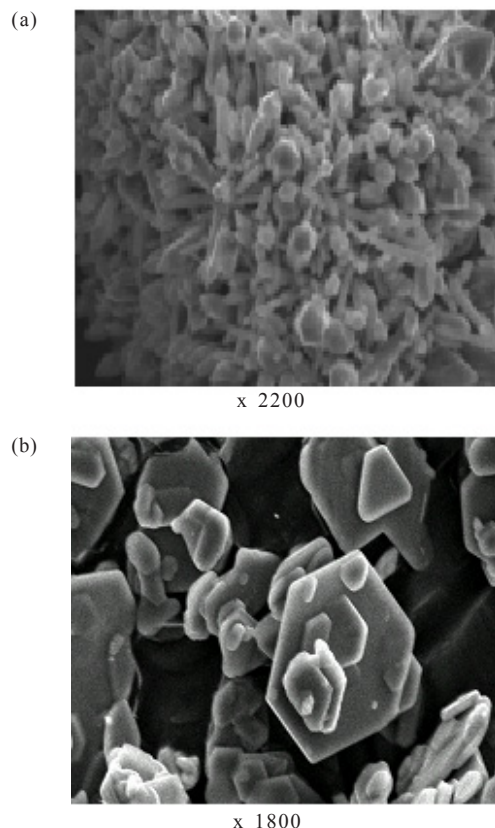


Figure 2. Scanning electron microscopy (SEM) photomicrograph of sub sample of the H8-syn (A) showing hexagonal rod crystals and of H14-syn (B) showing pseudo-hexagonal plates.

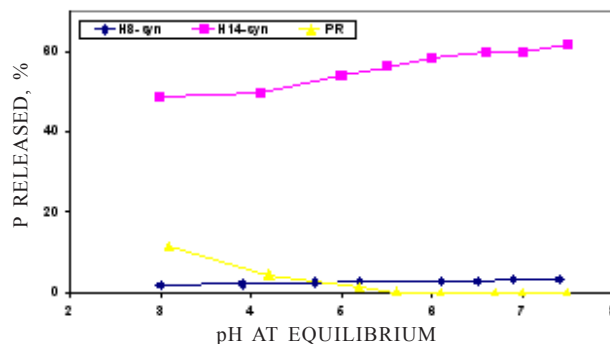


Figure 3. P released (%) from the reaction of H8-syn, H14-syn and Catalão PR as a function of the pH at equilibrium of a 0.01 mol L<sup>-1</sup> NaCl solution.

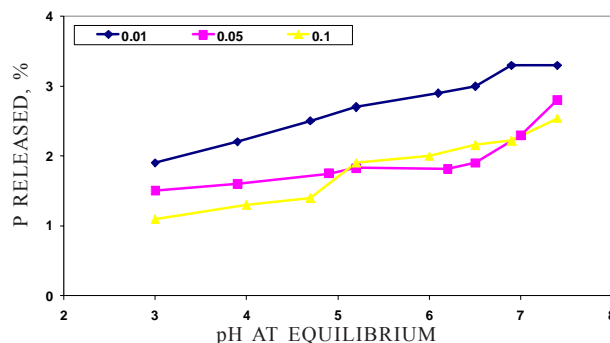


Figure 4. P released (%) from the hydrolysis reaction of H8-syn as a function of pH at equilibrium of NaCl solutions with concentrations of 0.01, 0.05 and 0.1 mol L<sup>-1</sup>.

increase in the relative amount of the ion pair  $\text{NaHPO}_4^-$  (Table 2) should be the explanation for the decrease in the activity of the orthophosphate ions after a certain pH. Results are in accordance with Sposito (1989), who mentioned that the activity of an ion tends to decrease with an increased ionic strength ( $\log f_i = -A z_i^2 \sqrt{\mu}$ ;  $a_i = c_i f_i$ , where:  $f_i$  = activity coefficient,  $A$  = parameter related to the dielectric constant,  $z_i$  = charge of the ion,  $\mu$  = ionic strength,  $a_i$  = ion activity,  $c_i$  = ion concentration). According to the formulas it is possible to infer that a higher  $\mu$  leads to higher negative log of  $f_i$ , or in other words, lower values of  $f_i$ , which will result to lower activity values. Consequently, the activity of the orthophosphate ions from the H8-syn and H14-syn

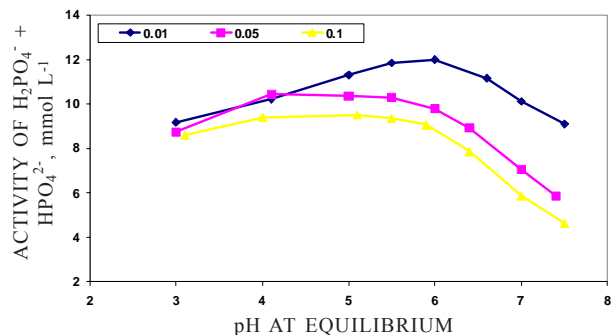


Figure 5. Activity of  $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$  from the hydrolysis reaction of H14-syn as a function of pH at equilibrium of NaCl solutions with concentrations of 0.01, 0.05 and 0.1 mol  $\text{L}^{-1}$ .

Table 2. Relative distribution of chemical species of P present in solution from the hydrolysis of the H14-syn, as a function of pH and NaCl concentration

Chemical specie	NaCl 0.01 mol $\text{L}^{-1}$							
	pH							
	3	4.1	5.0	5.5	6.0	6.6	7.0	7.5
$\text{HPO}_4^{2-}$	-	0.1	0.8	2.6	7.5	23.6	41.1	62.1
$\text{H}_2\text{PO}_4^-$	86.0	95.2	95.2	93.3	87.7	68.6	47.5	22.7
$\text{H}_3\text{PO}_4$	10.9	1.0	0.1	-	-	-	-	-
$\text{NaHPO}_4^-$	-	-	0.1	0.4	1.3	4.6	8.7	13.4
$\text{NaH}_2\text{PO}_4^-$ (aq)	2.7	3.4	3.4	3.3	3.1	2.8	2.1	1.0
$\text{Na}_2\text{HPO}_4$ (aq)	-	-	-	-	-	0.1	0.2	0.2
$\text{KHPO}_4^-$	-	-	-	-	-	0.2	0.4	0.5
$\text{KH}_2\text{PO}_4$ (aq)	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.1
$\text{FeHPO}_4^+$	0.1	-	-	-	-	-	-	-
$\text{FeH}_2\text{PO}_4^{2+}$	-	-	-	-	-	-	-	-
	NaCl 0.05 mol $\text{L}^{-1}$							
	pH							
	3.0	4.1	5.0	5.5	6.0	6.4	7.0	7.4
$\text{HPO}_4^{2-}$	-	0.1	1.0	3.2	9.2	19.1	42.4	55.3
$\text{H}_2\text{PO}_4^-$	83.1	90.4	90.3	87.4	79.9	66.4	37.0	19.2
$\text{H}_3\text{PO}_4$	9.5	0.8	0.1	-	-	-	-	-
$\text{NaHPO}_4^-$	-	0.1	0.4	1.2	3.3	7.4	16.2	22.3
$\text{NaH}_2\text{PO}_4^-$ (aq)	7.0	8.2	7.9	7.9	7.2	6.4	3.5	1.9
$\text{Na}_2\text{HPO}_4$ (aq)	-	-	-	-	0.1	0.3	0.6	0.8
$\text{KHPO}_4^-$	-	-	-	-	0.1	0.2	0.3	0.4
$\text{KH}_2\text{PO}_4$ (aq)	0.3	0.4	0.3	0.3	0.3	0.2	0.1	0.1
$\text{FeHPO}_4^+$	0.1	-	-	-	-	-	-	-
$\text{FeH}_2\text{PO}_4^{2+}$	-	-	-	-	-	-	-	-
	NaCl 0.01 mol $\text{L}^{-1}$							
	pH							
	3.1	4.0	5.1	5.5	5.9	6.4	7.0	7.5
$\text{HPO}_4^{2-}$	-	0.1	1.5	3.5	8.2	20.5	42.6	56.7
$\text{H}_2\text{PO}_4^-$	82.4	87.7	86.5	83.8	77.9	61.2	32.0	13.5
$\text{H}_3\text{PO}_4$	7.0	0.9	0.1	-	-	-	-	-
$\text{NaHPO}_4^-$	-	0.1	0.7	1.7	3.8	9.7	20.0	26.4
$\text{NaH}_2\text{PO}_4^-$ (aq)	10.2	10.9	11.0	10.6	9.6	7.9	4.1	1.7
$\text{Na}_2\text{HPO}_4$ (aq)	-	-	-	0.1	0.2	0.5	1.0	1.3
$\text{KHPO}_4^-$	-	-	-	-	0.1	0.2	0.3	0.4
$\text{KH}_2\text{PO}_4$ (aq)	0.3	0.3	0.3	0.3	0.2	0.2	0.1	-
$\text{FeHPO}_4^+$	-	-	-	-	-	-	-	-

(1) Adapted from results calculated by MINTEQA software (Allison et al., 1991).

tends to decrease when increasing the pH and/or the ionic strength of the solution.

The analysis of the residues in the filter paper after reaching the equilibrium pH suggests the presence of compounds very similar to H8 and amorphous strengite ( $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ ) in H8-syn and H14-syn, respectively (Figure 6). This is in accordance with the low hydrolysis of H8 and the chemical hydrolysis reactions suggested by Prochnow et al. (2003a) for both compounds.

In spite of using a simpler solution system than the soil solution, the information obtained in this study suggests that an increased P concentration for the hydrolysis of H8 and H14, as a function of an increase in the solution pH, does not necessarily lead to an intensified activity and consequently an increase in the bioavailability of phosphorus to plants, as suggested by Prochnow et al. (2003a). It can be suggested that

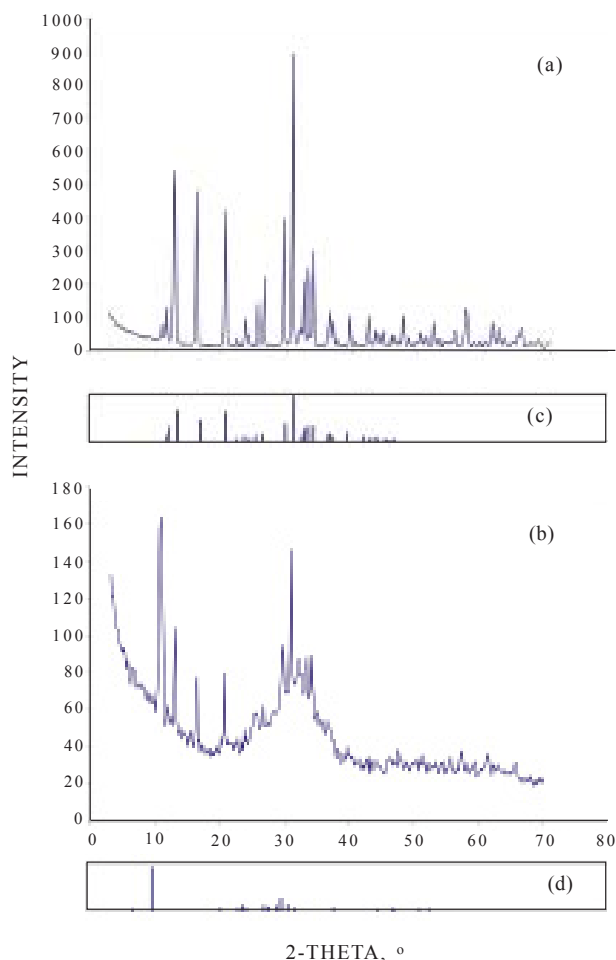
similar trends would be obtained in the soil system, once the exchangeable cationic concentration tends to increase with the pH. This can be important when agronomic data of P fertilizers with high contents of both of these Fe-K-P compounds are evaluated. Other studies with real soil solution enriched with Fe-K-P compounds should be carried out to gain further insights into this issue.

## CONCLUSION

Activity of orthophosphate ions derived from the hydrolysis of compounds of the type  $\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$  tends to decrease with a higher pH or ionic strength of the solution. Our results do therefore not confirm the hypothesis that these compounds are more plant available at a higher soil solution pH where the concentration of released orthophosphate ions is higher.

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**Figure 6. X ray diffractogram and powder diffraction file (PDF) data of the residues remaining in the filter paper after filtration of the solution of  $\text{NaCl}$   $0.01 \text{ mol L}^{-1}$  with pH 5 (original compounds: a = H8-syn, b = H14-syn; PDF file: c = H8, d = strengite).**



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