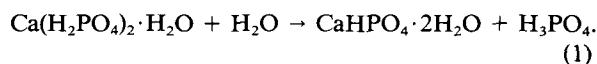


INFLUENCE OF RELATIVE HUMIDITY ON THE REACTION PRODUCTS OF PHOSPHATES AND NONCRYSTALLINE HYDROXIDES OF ALUMINUM AND IRON

Key Words—Aluminum, Infrared spectroscopy, Iron, Noncrystalline, Phosphate, Relative humidity.

Aluminum and iron in noncrystalline constituents in soils play a major role in phosphate fixation. Noncrystalline aluminum and iron hydroxides have often been used as model materials of these soil constituents. Previously, phosphate sorption on noncrystalline aluminum and iron hydroxides were carried out in suspension (Nanzyo, 1984, 1986); however, phosphate fertilizers and soils ordinarily react in much less aqueous environments. Lehr *et al.* (1959) reported that 27–34% of monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) was converted to dicalcium phosphates at 0.5–1.0 moisture equivalent in soils. Reaction of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to give dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) can be formulated as follows (Lindsay, 1979):



Released H_3PO_4 must react with an adsorbent to give another product, depending on the adsorbent. In this note, the products of moisture-dependent reactions of noncrystalline hydroxides of aluminum and iron and four phosphates, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, monomagnesium phosphate dihydrate ($\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$), and dimagnesium phosphate trihydrate ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) are presented. An infrared absorption spectrum of the small amount of phosphate in the reaction mixture was obtained by subtracting the diffuse reflectance infrared (DRIR) spectrum of the control adsorbent from that of the phosphated adsorbent. This infrared spectroscopic method was useful for identifying the reaction product especially when it was present as a surface complex or as a material amorphous to X-rays. If the product was a mixture of several components, subtracting the spectrum of one component from that of the mixture allowed the other component to be identified.

EXPERIMENTAL

Noncrystalline aluminum hydroxide and noncrystalline iron hydroxide were prepared as reported by Nanzyo (1984, 1986). Commercially available, guaranteed grade $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and

$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ were used. These phosphates gave the expected X-ray powder diffraction peaks and infrared spectra reported in the literature (Lehr *et al.*, 1967). $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by dissolving magnesium carbonate in phosphoric acid at 80–90°C, followed by cooling and crystallization in ethyl acetate (Belopolsky *et al.*, 1950). The Mg and P contents were 9.72 and 24.0%, respectively. The calculated Mg and P contents for $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ were 9.56 and 24.36%, respectively. A powdery mixture of 0.3 g of noncrystalline material and 15 mg of a phosphate salt (weight ratio = 20:1, the amount of noncrystalline materials in soil is typically much larger than that of phosphate) was prepared using an agate mortar. After the material had been mixed and allowed to stand for 3 and 10 days at relative humidities (RH) of 30–40% and 96–100% and in 1 ml of water, it was dried under reduced pressure and subjected to X-ray powder diffraction (XRD) and DRIR analysis. The temperature was controlled at 25°C. Details of the XRD and DRIR analyses were reported by Nanzyo (1984). The average water contents at RHs of 30–40% and 96–100% are shown in Table 1.

Difference DRIR spectra were obtained by the following procedure. First, the amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ formed from $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at RH = 96–100% was estimated stoichiometrically according to Eq. (1). Next, the intensities of the absorption bands of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were adjusted in small increments by trial and error, using a computer-equipped FT-IR spectrometer. Spectral subtraction was carried out according to the following equation

$$\text{Spectrum A} - (\text{K Spectrum B}),$$

where spectra A and B are those of the phosphate phase produced and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, respectively, in a mixture containing noncrystalline Al or Fe hydroxides. Various values of K were tried for the several products described in this paper.

RESULTS

The DRIR spectra of the products formed from Mg and Ca phosphates and noncrystalline aluminum and

Table 1. Water contents (wt. %) of the powder mixtures of noncrystalline hydroxides and phosphates.¹

Relative humidity (%)	Reaction period (days)	Noncrystalline aluminum hydroxide	Noncrystalline iron hydroxide
30-40	3	14	13
	10	15	14
96-100	3	30	24
	10	39	25

¹ 105°C oven-dry basis.

iron hydroxides were the same as those of the sorption products prepared from sodium phosphate solution, irrespective of cation species, except that $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was partly formed from $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at an RH of 96–100%. The formation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ from $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was favored at an RH of 96–100%, but not at an RH of 30–40%, nor in water. At an RH of 96–100%, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ disappeared in 3 days, whereas part of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ remained after 10 days, probably because of their different solubilities. Results are summarized in Tables 2 and 3.

Products from $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

In 10 days, at an RH of 30–40%, the XRD intensities indicated that most of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ remained in the mixtures containing the noncrystalline aluminum and iron hydroxides.

At an RH of 96–100%, the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ inconspicuously dissolved to give $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the mixtures containing noncrystalline aluminum and iron hydroxides. The XRD peaks of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (11.8, 5.86, 3.88 Å, etc.) disappeared (Figure 1), and the XRD peaks of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (7.62, 4.25, 3.06 Å, etc.) appeared. In the DRIR spectra of the product in the mixture containing noncrystalline aluminum hydroxide (Figure 1), an absorption band at 1135 cm^{-1} having shoulders on both sides was observed. This spectrum is different from that of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ which has sharp absorption bands at 1220, 1130, 1070, 990, and 870 cm^{-1} ; thus, other products, amorphous to X-rays, appear to have formed. By subtracting the DRIR spectrum of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the mixture containing noncrystalline aluminum hydroxide from that of the

products, a spectrum similar to that of noncrystalline aluminum phosphate (Nanzyo, 1984) was obtained. In that spectrum a broad absorption band at 1135 cm^{-1} and a shoulder at 1040 cm^{-1} were observed (Figure 1). In the DRIR spectra of the product in the mixture containing noncrystalline iron hydroxide, several absorption bands between 990 and 1130 cm^{-1} were observed at an RH of 96–100% (Figure 2). From an analysis of the spectra, similar to that described above, the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ appeared to have dissolved inconspicuously from the mixture containing noncrystalline iron hydroxide to yield $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and a mixture of noncrystalline iron phosphate and a binuclear surface complex (Nanzyo, 1986). The addition of water (1 ml) to these reaction mixtures gave the same products as those formed in water after standing for 3 days.

According to Lindsay (1979), $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ in fertilizer granules dissolves initially to give $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ which later converts to more stable dicalcium phosphate with time. In the present experiment, only $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was detected after 10 days in the mixtures containing noncrystalline aluminum and iron hydroxides. The reaction of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to give $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ can be described as in Eq. (1). Released H_3PO_4 was apparently sorbed on noncrystalline aluminum hydroxide to give noncrystalline aluminum phosphate and was sorbed on noncrystalline iron hydroxide to give a mixture of noncrystalline iron phosphate and binuclear surface complex.

IR bands related to the P–O stretching vibration of phosphate sorbed on noncrystalline iron hydroxide depends on pH; at pH 12.3, the IR bands were observed at 1110 and 1010 cm^{-1} , and the splitting width of the two bands became small with decreasing pH; at pH 2.3, one broad IR band was observed at 1060 cm^{-1} (Nanzyo, 1986). The IR spectrum of the phosphate materials sorbed on noncrystalline iron hydroxide (Figure 2), contained two bands at 1110 and 1020 cm^{-1} . Positions of these bands corresponds to the bands at about neutral pH. After the addition of 6 ml of water to the reaction mixture containing noncrystalline iron hydroxide, the pH was 6.9. Absorption bands of noncrystalline aluminum phosphate depend only slightly on pH (Nanzyo, 1984).

In water, the products were amorphous to X-rays in the mixtures containing noncrystalline aluminum and

Table 2. Phosphates detected in the mixtures of noncrystalline aluminum hydroxide and calcium and magnesium phosphates under various relative humidities in 10 days.

Phosphates	Moisture		
	RH = 30-40%	RH = 96-100%	In water
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, NAP ¹	NAP
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, NAP	NAP
$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	NAP	NAP
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, NAP	NAP

¹ NAP = noncrystalline aluminum phosphate.

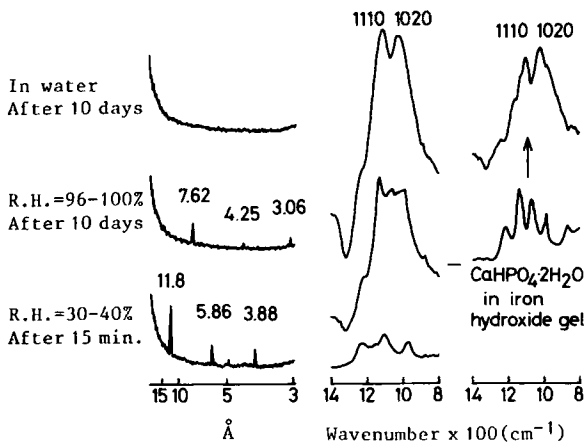


Figure 1. X-ray powder diffractograms of the powder mixtures of monocalcium phosphate monohydrate and noncrystalline aluminum hydroxide (alumina gel) and diffuse reflectance infrared spectra of the phosphate phase.

iron hydroxides. From the differential DRIR spectra, the product in the mixture containing noncrystalline aluminum hydroxide appeared to be noncrystalline aluminum phosphate; those in the mixture containing noncrystalline iron hydroxide appeared to be mixtures of noncrystalline iron phosphate and binuclear surface complex.

Products from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

At an RH of 30–40%, most of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ remained after 10 days. With increasing time and moisture, the amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ decreased. In water, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ disappeared, whereas at an RH of 96–100%, part of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ remained in the mixtures containing noncrystalline aluminum and iron hydroxides after 10 days. The product in the mixture containing noncrystalline aluminum hydroxide was noncrystalline aluminum phosphate; that in the mixture containing noncrystalline iron hydroxide was a mixture of noncrystalline iron phosphate and binuclear surface complex.

Products from $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

At an RH of 30–40%, most of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ remained in the mixtures containing noncrystalline

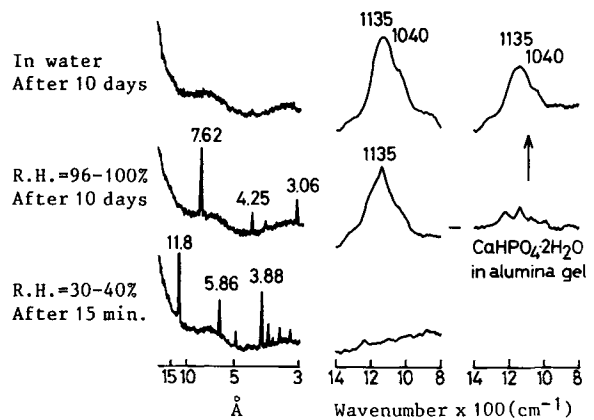


Figure 2. X-ray powder diffractograms of the powder mixtures of monocalcium phosphate monohydrate and noncrystalline iron hydroxide (iron hydroxide gel) and diffuse reflectance infrared spectra of the phosphate phase.

aluminum and iron hydroxides after 10 days. At an RH of 96–100%, the $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ disappeared completely in 3 days. The products were the same as those formed in the reactions with $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. No incongruent dissolution was noted as was observed for $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at an RH of 96–100%.

Products from $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$

The reactivity of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ with noncrystalline aluminum and iron hydroxides was about the same as that of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and the products were the same as those from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

DISCUSSION

Moisture content influenced the reaction of noncrystalline hydroxides of aluminum and iron and phosphates of calcium and magnesium. At an RH of 96–100%, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ incongruently dissolved to give $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, even in the presence of noncrystalline hydroxides of aluminum and iron, which are highly reactive with phosphate. Thus, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ apparently formed from superphosphate and can remain in soils having high phosphate-retention capacity for about 10 days by controlling the moisture content of the soils. The analogous incongruent reaction was not observed in the mixture containing magnesium phosphate.

Table 3. Phosphates detected in the mixtures of noncrystalline iron hydroxide and calcium and magnesium phosphates under various relative humidities in 10 days.

Phosphates	Moisture		
	RH = 30–40%	RH = 96–100%	In water
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, AIP, BSC	NIP, ¹ BSC ²
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, NIP, BSC	NIP, BSC
$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	NIP, BSC	NIP, BSC
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, NIP, BSC	NIP, BSC

¹ NIP = noncrystalline iron phosphate.

² BSC = binuclear surface complex.

It takes several years for noncrystalline phosphate of aluminum and iron to crystallize at room temperature (Hsu, 1982, 1983). Phosphate fertilizers are ordinarily applied to soils every year. Therefore, the role of these noncrystalline phosphates is important in crop production. The exact species of noncrystalline aluminum and iron phosphate would be different in environments having different Al:P and Fe:P molar ratios and water contents. In the present experiment, the exact species of noncrystalline aluminum and iron phosphate that formed were not ascertained. In typical arable land, the reaction product of soils and fertilizers are difficult to identify by XRD, possibly due to the noncrystalline nature of the product or to the small content of the product in soils. The combination of DRIR and difference DRIR is a method that is useful for elucidating such problems.

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