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Study on structural characteristics of pillared clay modified phosphate fertilizers and its increase efficiency mechanism*

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Abstract: Three types of new high-efficiency phosphate fertilizers were made when pillared clays at certain proportions were added into ground phosphate rock. Chemical analyses showed that their soluble phosphorus content decreased more than that of superphosphate. Pot experiment showed that, under equal weights, the new fertilizers increased their efficiency by a large margin over that of superphosphate. Researches on their structures by means of XRD, IR and EPR spectrum revealed that their crystal structures changed considerably, improving their activity and preventing the fixation of available phosphorus in the soil, and consequently, greatly improved the bioavailability and became the main cause of the increase of biomass.

Key words: High-efficiency phosphate fertilizers, Structures, Pillared clay, Pot experiment
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INTRODUCTION

Phosphorus deficiency is a common phenomenon in China's soils. Over 67% of croplands have this problem in varying degrees. The situation is worse in the red soil regions where the high contents of Fe, Al in the soil tend to fix more phosphorus when common phosphate fertilizers are applied, thus reducing the availability (Lu and Liao, 1997). China's phosphors mines produce mostly medium and low-grade phosphorus, it is therefore important to upgrade their output of phosphorus and make it as efficient as chemically produced fertilizers (Wang, 1998). The key to this problem lies on these aspects: to activate the phosphorus, to build up its anti-fixation ability and thus improve its efficiency. We conducted experiments under laboratory conditions using organic and inorganic modified materials to activate ground phosphate rock, and obtained several high-efficiency phosphate fertilizers (HEPFs), whose physical and chemical characteristics obviously changed. They showed improved efficiency both in acid red soil and alkaline soil and promised a bright future in application.

MATERIALS AND METHODS

Fertilizer material for experiment

The phosphate rock experimented on was from Kunyang (Yunnan Province, China) with phosphorus content of 27.5%, while the content of available phosphorus in common superphosphate is 16%, nitrogen in urea 46%, K_2O in potassium chloride 60%. Three additives are organic pillared montmorillonite OrPM, organic-inorganic pillared montmorillonite OIPM and inorganic pillared montmorillonite IPM. The processing of IPM, OrPM, OIPM and HEPFs was as follows:

(1) Inorganic pillared montmorillonite IPM:

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Montmorillonite from Heping, Guangdong Province in China, was purified, dried, and pulverized to pass 75 μm mesh sieve, to prepare IPM (Wu *et al*., 2001). Montmorillonite (CEC (Cation Exchange Capacity)=0.57 mol/kg) was modified to Na-montmorillonite (CEC increased to 0.86 mol/kg), to obtain grains less than 2 μm, prepared for a 4.5 g/L suspension. Then, 50 ml of $AlCl_3$ solution was prepared, agitated continuously, and 1 mol/L Na_2CO_3 solution was slowly added at 60 °C, until a final OH/Al ratio of 2.4 was reached. The resulting solution was allowed to react continuously for 2 h and then stored at 60 °C for 2 d. Then, under continuous agitation, the pillared reagent was slowly put into Na-montmorillonite serosity to obtain a ratio of 10 cmol/kg of montmorillonite. The reaction continued for 2 h, after which it was left for 2 d. The resulting IPM was centrifuged and washed until Cl^- could not be detected, then dried at 80 °C.

(2) Organic pillared montmorillonite OrPM: Montmorillonite was modified to Na-montmorillonite, prepared for a 4.5 g/L suspension. Then, 50 ml of humic acid solution was slowly added into Na-montmorillonite serosity at 60 °C. Then, under continuous agitation, the reaction continued for 2 h, after which it was left for 2 d, then dried at 80 °C.

(3) Organic-inorganic pillared montmorillonite OIPM: The OIPM was prepared by humic acid and IPM. We put the humic acid solution (1.0 g/L) into the IPM suspension to make the amount of organic compound correspond with that CEC of montmorillonite, followed by 4 h agitation. The suspension was then centrifuged, washed several times, and dried at 80 °C.

(4) Partially acidified modified phosphate fertilizer: 15 g OrPM was mixed with 100 g phosphate rock, to react with 15 g concentrated sulfuric acid then air-dried to get GX1 (Liao *et al*., 2003). GX2 and GX3 were made using the same methods by mixing phosphate rock with additives OIPM and IPM respectively. The superphosphate treated with additives was named CK1 and the superphosphate treated without additives was named CK2.

Soils for experiment

The to be experimented on acid soil was collected from South China Agricultural University, Shipai, Guangzhou, and was lateritic red soil derived from granite parent material: pH 5.01 (water:soil=1:10), organic matter 0.137%, total N 510 mg/kg, total K (K_2O) 5000 mg/kg, total P (P_2O_5) 271 mg/kg, available P (P_2O_5) 3.5 mg/kg.

Pot experiment

Five treatments and three repetitions were designed for the partially acidified modified phosphate fertilizer pot experiment. The N (urea) was applied at 70 mg N/kg soil and K (KCl) at 95 mg K_2O/kg soil, all of which were applied once in full amount as base fertilizer. Superphosphate (named CK1), CK2, GX1, GX2, and GX3 were respectively applied to treatments 1 through 5 all at the ratio of 43.33 mg/kg soil. Corn was planted on Mar 20, 2003 at 3 plants a pot. On Apr 23, 2003 corn seedlings were cut down at soil-surface level and fresh weights were taken. The growth period was 34 d.

Testing methods and conditions

The contents of soluble phosphorus and available phosphorus in these HEPFs were extracted and determined by distilled water and neutral ammonium citrate respectively. The amount of total phosphorus was determined by H_2SO_4, H_2O_2 digestion and vanadium molybdenum yellow chromometry, The XRD patterns and *d* values were measured and determined by using the X-ray Powder Diffraction instrument, Model D/MAX 1200. IR analyses were made by the Perkin-Elmer 1725X, FT-IR. Sample weighted 1 mg, squashed with KBr. EPR was Bruker ECS-106 Electronic Paramagnetic Resonance from Germany, the working frequency was 9.76 GHz, the scale of scanning magnetic field was 6000×10^{-4} T.

RESULTS AND DISCUSSION

Contents of available phosphorus and water soluble phosphorus in HEPFs

Table 1 shows the contents of available P and soluble P in the three types of partially acidified HEPFs for comparison with those in the acidified P fertilizer CK2.

Table 1 shows that the contents of soluble P in these HEPFs decreased by a wide margin (respectively by 5.1%, 16.5% and 15.8%), while the range of decrease in available P is not large (only 1.3%, 0.8% and 4.8%). There are three possible reasons for the results. One was that the additives had relatively reduced the volume of H_2SO_4 reacting with phosphate rock, and consequently reduced the free $H_2PO_4^-$ produced. Second is that the additives combined with phosphorus during the reaction to form a new state with weak solubility but its availability still remained high. The third is that the presence of additives seemingly reduced the contents percentage of phosphorus and thus reduced the content of total phosphorus correspondingly.

Results of pot experiment with acid red soil

As phosphorus is easily fixed into the soil, thus reducing its availability, the effects of phosphate fertilizers depend more on their biological availability than on their chemical availability. In Table 2, CK2 has 9.22% biomass increase than CK1, again, three HEPFs have over 20% biomass increase than CK2, and over 30% than CK1. These data indicated that phosphorus in the three fertilizers had very high bio-availability, among which, GX2 was the best, with increase of 44.58% and 32.38% compared with CK1 and CK2.

Absorption capacity of phosphorus in aerial parts of differently treated corns

Table 3 shows the phosphorus contents and absorption capacity of corns in each treatment. The table shows that treatment GX2 had the highest phosphorus content and highest phosphorus absorption capacity, which corresponds to its highest biomass. It showed, therefore, that this treatment promoted the absorption of phosphorus and increased the output. Treatments GX3 and GX1 came next. On the contrary, treatment SP (CK1), common superphosphate, had the lowest phosphorus content and the lowest phosphorus absorption capacity and the output among the treatments. Compared with treatment SP (CK1) and CK2, treatment GX2 increased remarkably (0.05) in both phosphorus content and phosphorus absorption capacity.

XRD analyses of HEPFs

Fig.1 of the X-ray diffraction (XRD) patterns of phosphate rock and five phosphate fertilizers shows that the content of carbonate fluorapatite in phosphate rock exceeds 80%, and that there is less than 20% of quartz (three characteristic diffraction peaks 0.42782, 0.33532, 0.l84 nm). The form of the apatite diffraction peak 0.280 nm has important relation with direct application of phosphate rock (Li *et al.*, 1992). The content of available phosphorus is inversely proportional to the intensity of the diffraction peak, directly proportional to the full width at half maximum (FW-

Table 1 The available and soluble phosphorus in four phosphate fertilizers

Type of phosphate fertilizer	CK2	GX1	GX2	GX3
Soluble phosphorus (P_2O_5%)	16.62	15.77 (−5.1%)	13.88 (−16.5%)	13.99 (−15.8%)
Available phosphorus (P_2O_5%)	19.45	19.20 (−1.3%)	19.29 (−0.8%)	18.52 (−4.8%)
Soluble P/available P (%)	85.45	82.14	71.95	75.54

Percentage in bracket indicates the changes to CK2

Table 2 The potted plant biomass of different phosphate fertilizer treatments

Treatment		Common SP (CK1)	CK2	GX1	GX2	GX3
Biomass (g/Pot)		11.17 c	12.20 b	15.58 a	16.15 a	14.65 ab
Comparisons of biomass (±%)	CK1	100	9.22	39.48	44.58	31.15
	CK2	−8.44	100	27.70	32.38	20.08

Dancan's multiple comparison method is used for the data multiple comparison. P=0.05, mean values within a column followed by the same letters are not significantly different

Table 3 Phosphorus absorption capacity in aerial parts of different treatment corns

Treatment	Common SP (CK1)	CK2	GX1	GX2	GX3
Phosphorus content (%)	0.145 b	0.146 b	0.155 ab	0.164 a	0.163 a
Absorption capacity (P mg/Pot)	1.770 b	1.825 b	2.372 a	2.493 a	2.135 ab

Dancan's multiple comparison method is used for the data multiple comparison. P=0.05, mean values within a column followed by the same letters are not significantly different

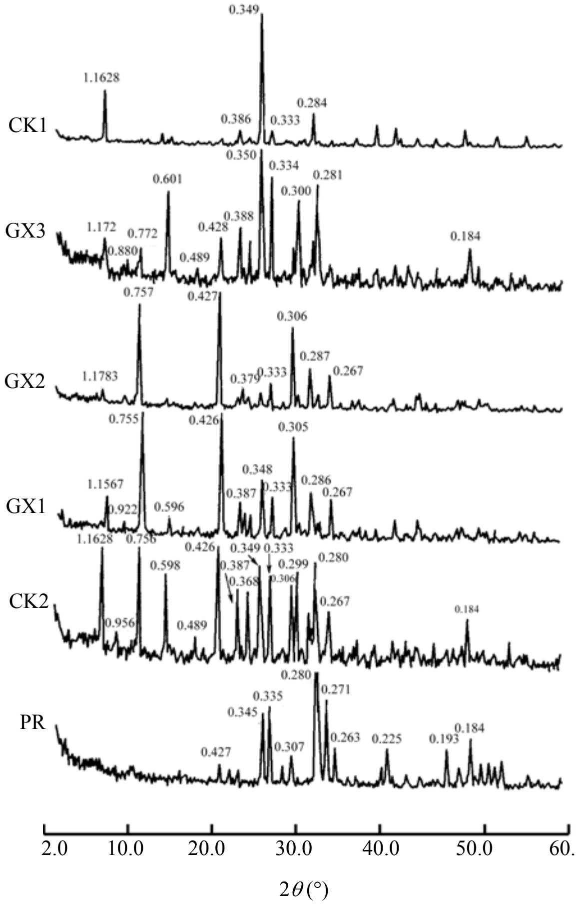

Fig.1 X-ray diffraction (XRD) patterns of phosphate rock and five phosphate fertilizers

HM), and is inversely proportional to the crystallinity. As the Kunyang phosphate rock crystallizes very well at diffraction peaks 0.28068, 0.27813 nm, it is therefore not suitable for direct application. In contrast HEPFs, after different treatments had very different diffraction patterns. XRD showed that fertilizers CK2, GX1, GX2 and GX3 all had $Ca(H_2PO_4)_2{\cdot}2H_2O$, $CaHPO_4{\cdot}2H_2O$, gypsum and quartz. We here focus on $Ca(H_2PO_4)_2{\cdot}2H_2O$ and $CaHPO_4{\cdot}2H_2O$ to discuss the diffraction characteristics of these two different phosphorus forms. CK2, $Ca(H_2PO_4)_2{\cdot}2H_2O$ has 7 characteristic diffraction peaks 1.1628, 0.5985, 0.4889, 0.3873, 0.368, 0.3336, and 0.2998 nm (Lai and Eberl, 1986). Whereas, in GX1, GX2 and GX3, has respectively 5, 3, and 4 peaks, fewer peaks and poorer crystallinity compared to CK2. In the three new fertilizers, the number of pattern peaks of $CaHPO_4{\cdot}2H_2O$ remains at the same 4 peaks (approximately near 0.756, 0.427, 0.306 and 0.268 nm), but there is a slight decrease in crystallinity. This may possibly be due to the stronger combining capacity of HPO_4^{2-} and Ca^{2+} so that the organic-inorganic additives cannot reduce $CaHPO_4{\cdot}2H_2O$'s characteristic peaks. The adding of these additives, however, has attracted or combined part of the Ca^{2+} to their surface. and has reduced the attraction of ionic bonds between Ca^{2+} and $H_2PO_4^-$ or HPO_4^{2-}, thus decreasing the number of characteristic peaks of $Ca(H_2PO_4)_2{\cdot}2H_2O$ and $CaHPO_4{\cdot}2H_2O$'s crystallinity. Comparison of the XRD pattern of HEPFs with that of SP showed that the content of $Ca(H_2PO_4)_2{\cdot}2H_2O$ in SP is more than 80%; the content of $CaHPO_4{\cdot}2H_2O$ in SP less than 20%; the content of $Ca(H_2PO_4)_2{\cdot}2H_2O$ in HEPFs is remarkably less than 80% and the content of $CaHPO_4{\cdot}2H_2O$ in HEPFs is more than 20%.

Regarding the different diffraction intensities of $Ca(H_2PO_4)_2{\cdot}2H_2O$, CK2 is much stronger than the other three types. Next comes GX1. GX2 and GX3 are the weakest without distinct difference. In the four types of fertilizers, CK2 has the most $Ca(H_2PO_4)_2{\cdot}2H_2O$, followed by GX1. The results coincide with the chemical analyses, showing that the content of soluble phosphorus in CK2 was the highest, GX1 the second, and GX2 and GX3 the lowest with little difference.

IR analyses of HEPFs

Fig.2 shows the IR pattern of phosphate rock and 5 types of phosphate fertilizers. It is obvious in the IR that the phosphate rock from Kunyang is typical of carbonate-fluorapatite (Peng *et al.*, 1986). The elastic vibrating absorption pattern of water in phosphate rock is 3442 cm^{-1}; 1455 cm^{-1}, 1430 cm^{-1} are the anti-symmetrical elastic vibrating ν_3 absorption patterns of CO_3^{2-} in phosphate rock; 865 cm^{-1} is the elastic vibrating ν_2 absorption patterns of CO_3^{2-}; 1098 cm^{-1}, 1048 cm^{-1} are the anti-symmetrical elastic vibrating ν_3 absorption patterns of PO_4^{3-} in phosphate rock; 966 cm^{-1} is the symmetrical elastic vibrating ν_1 absorption pattern of PO_4^{3-}; 606 cm^{-1}, 569 cm^{-1} are the bending vibrating ν_4 absorption patterns of PO_4^{3-}; 472 cm^{-1} is the elastic vibrating ν_2 absorption pattern of PO_4^{3-} (Chesworth *et al.*, 1987; Kithome *et al.*, 1998). After different treatments, the IR pattern of these phosphate fertilizers underwent great changes:

(1) There began to appear a hydroxylate elastic

vibrating absorption pattern 3549 cm^{-1}.

(2) The absorption patterns of CO_3^{2-} all disappeared.

(3) PO_4^{3-}'s absorption patterns changed greatly, corresponding characteristic absorption patterns of $H_2PO_4^-$ (1666 cm^{-1}, 677 cm^{-1}, 512 cm^{-1}) and HPO_4^{2-} (1621 cm^{-1}, 601 cm^{-1}) began to appear. The IR pattern of SP was mainly the characteristic absorption patterns of $H_2PO_4^-$.

EPR analyses of HEPFs

Electronic Paramagnetic Resonance (EPR) is usually used to research complex with isolated electrons. EPR spectra can provide some information such as the coordinate number, value state, local symmetry, concentration and crystal field parameter of impurity elements with paramagnetic center, and explain some physical properties. EPR spectra consist of three groups of parameters: (1) fine structural parameter (initial split); (2) *g* parameter (the split caused by magnetic field action); (3) ultrafine structural parameter (the split caused by interaction with nuclear magnetic moment).

Microncontent transitional element and organic and inorganic free radicals, which exist in fertilizers and vegetable. These paramagnetic centers are EPR technology research subjects, among which Fe^{3+} and Mn^{2+} are the most important.

Fig.3 is the EPR spectra of phosphate rock and HEPFs. In Fig.3, rhombic symmetry Fe^{3+} (g=4.216)

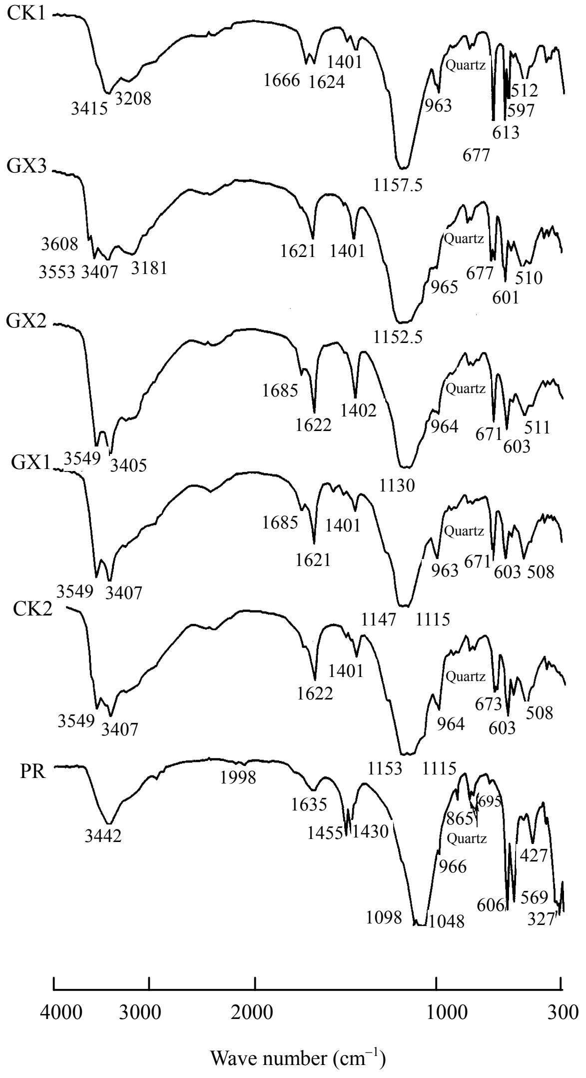

Fig.2 IR of phosphate rock and five phosphate fertilizers

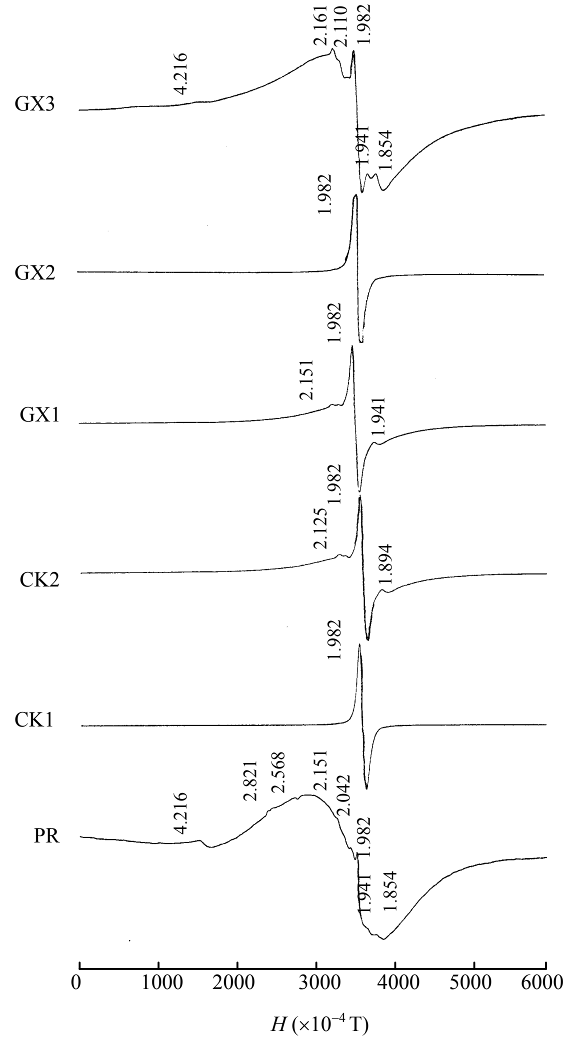

Fig.3 EPR spectra of phosphate rock and modified phosphate fertilizers

spectrum peak and 5 ultrafine structural spectrum peaks (*g*=2.151, 2.042, 1.982, 1.941, 1.854) appear in the EPR spectra of phosphate rock. There is only a sharp peak of cavity-color central coupling free radical (*g*=1.982) in the EPR spectra of superphos phate CK1. Comparison of EPR spectra of superphosphate and that of phosphate rock revealed that there was no Fe^{3+} peak in the EPR spectra of other HEPFs, except for a small rhombic symmetry Fe^{3+} (*g*=4.216) peak appearing in GX3. In addition, after modifying the structure of phosphate rock, the ultrafine structural of the spectrum peaks of Mn^{2+} in HEPFs disappeared, and only about 2 to 3 peaks could be seen, indicating that after modification, the phosphate rock structure tended to be disordered.

Fig.4 is the EPR spectra of corn fertilized with superphosphate and modified phosphate fertilizers. Only Fe^{3+} (*g*=2.350) and a few Mn^{2+} peaks (*g*=2.146, 1.987) appeared, but no rhombic symmetry Fe^{3+} (*g*=4.2) peaks appeared in the EPR spectra of HEPFs. Six ultrafine structural spectrum peaks (*g*=2.199, 2.135, 2.047, 1.996, 1.918, 1.862) of Mn^{2+} appeared in GX1, while peak of Cu^{2+} (*g*=2.524) appeared in GX3.

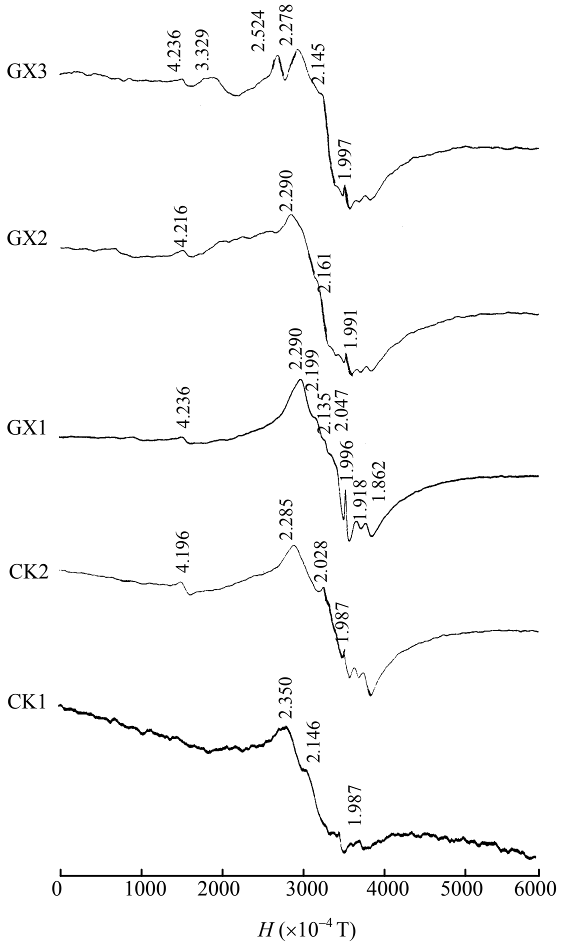

Fig.4 EPR spectra of corn with superphosphate and modified phosphate fertilizers

EPR spectra of the plant sample indicated HEPFs application can improve equalization absorption and tend to disorder the distribution of Fe^{3+}, Mn^{2+} in plant. The peak (*g*=4.2) appeared in all EPR spectra of HEPFs, and the corresponding rhombic symmetry Fe^{3+} is probably equal to the chelate Fe chlorophyll, although there is no such kind of Fe in CK1, when superphosphate is used as fertilizer.

Mechanism analyses of increasing efficiency of HEPFs

The increase of biomass in CK2 over that in CK1 as shown in Table 3 may be due to their different contents of available phosphorus. After the treatments of the three types of HEPFs, their biomasses increased significantly compared with the biomasses after treatment of CK2. But their contents of available phosphorus were actually lower than that of CK2; apparently, this was something that could not be interpreted by the contents of available phosphorus. This phenomenon in which the content of available phosphorus decreased with increasing output indicated that different forms of phosphorus inside the available phosphorus contribute differently to the effects of phosphorus fertilizers. The reinforcement of certain component with high capacity to resist the fixation of phosphorus into soil may compensate for the relatively low availability of phosphorus. In Table 4, the significant increases of plant phosphate contents and their absorption capacity in three types of HEPFs suggest that the effectiveness of HEPFs has also much improved. The speed of P fixation into the soil differs with different phosphate forms. It can be noted from both the chemical analyses and crystal structure analyses that ordinary acidified phosphorus has more free $H_2PO_4^-$ ions in its available phosphorus. When applied, these free ions have more chance to react with Fe, Al, etc, and then fix faster. In the three HEPFs, however, $H_2PO_4^-$ and HPO_4^{2-} may combine with Ca^{2+} or the additives surface to form poly-complex compound, or may reduce the fixation of available phosphorus by means of surface absorption or enveloping so that their bio-availability increased.

Phosphorus can be easily fixed in soils and thus become inefficient. The effectiveness of a type of phosphate fertilizer, therefore, does not wholly depend on its chemical availability, as chemical availability does not equal biological availability. The changed forms of phosphorus after additive treatments strengthen the ability to resist fixation. The assortment of different forms of phosphorus has formed a reliable "column orientation balance" (Liao *et al.*, 1999) which is better adapted to the needs of crops and will enhance the fertilizer use efficiency. Meanwhile, the adaptation of different type of P can improve equalization absorption and make the distribution of Fe^{3+}, Mn^{2+} in plants tend to be orderly.

The three fertilizers, though lower in contents of available phosphorus, had greater output than CK2, and even greater output than SP. This shows that they had better phosphorus use efficiency. Furthermore, as the inclusion of additives effectively reduced the actual consumption of phosphorus (less than 85%), the high efficiency is even more evident. The efficiency is closely related to a number of specific components, especially to the one or several forms of available phosphorus existing inside. It is owing to these phosphate forms, different from acidified P fertilizer, that the ability of anti-fixation is fortified. Deep researches into the properties of these effective components and proper production conditions will obviously be important for developing new, high efficiency phosphate fertilizers and improve phosphate fertilizer use efficiency.

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