Technology for the solubilization of phosphate rock and its advantages—Phosphate rock solubilization by low-temperature calcination

Nakamura S.

Japan International Research Center for Agricultural Sciences (JIRCAS), Tsukuba, Japan

INTRODUCTION

The effect of phosphate rock (PR) direct application is inferior to that of water-soluble P fertilizer; several biological, chemical, and physical means can be used to enhance the availability of PR to plants (FAO, 2004; Nakamura *et al*., 2013). Among presented technologies for PR solubilization, chemical and physical methods will be processed in fertilizer plants, while the biological one such as PR added-composting can be carried out by farmers by themselves. And therefore, it seemed not applicable technologies for small-scale agronomies.

PR elution characteristics are known to be substantially improved by high-temperature calcination (Bolan *et al*., 1993; Ando, 1987). The high-heat processed phosphorus (P) fertilizer is widely used and is called "calcinated phosphate fertilizer" and/or "fused phosphate fertilizer."

Calcinated phosphate fertilizer is the P fertilizer that has improved citric acid solubility by the defluorination process with high-heat processing at 1300 °C and addition of Na_2O, leading to the production of α-tricalcium phosphate and, partially, rhenanites ($CaNaPO_4$). Fused phosphate fertilizer is obtained by melting some of the components in addition to PR (Bolan *et al*., 1993). In Japan, fused magnesium phosphate fertilizer is widely used.

However, these calcination and fusion treatments need costly facilities and advanced techniques like for some chemical procedures for PR solubilization. They cannot be applicable to farmers in the developing countries. However, several studies have suggested low-temperature calcination enhanced low-grade PR solubility, which might allow the development of farmer-applicable technology for Burkina Faso PR (BPR) solubilization.

Therefore, this study investigated the effect of low-temperature calcination on the improvement of BPR solubility. The applicability of low-temperature calcination technology by using Kun-tan (biochar) prepared using indigenous saw dust and rice husk was also evaluated.

METHODS
Material and Calcination procedure
In our study, PR produced in Kodjari, Burkina Faso (BPR), was investigated. BPR mainly

consists of Fluorapatite ($Ca_5(PO_4)_3F$) and Quartz(SiO_2), and the P_2O_5 contents in BPR was 34.1% (Nakamura *et al*, 2015).

The BPRs were calcinated using Muffle furnace for 1, 2, 4, and 8 h at 6 levels of temperature from 100 °C to 600 °C at 100 °C intervals. After calcination, BPR was placed in a desiccator for cooling. Then, the calcinated BPR was analyzed as low-temperature calcinated PR sample (LTC-BPR).

Chemical analysis

The solubility of BPR and LTC-BPR was analyzed by water extraction and 2 % citric acid extraction. About 25 mL of the two solvents were added to 0.25 g of samples. After 16 h of shaking, the samples were centrifuged for 5 min at 3000 rpm. The P contents in the supernatant were determined using the molybdenum blue method by adding ascorbic acid. The absorbance was detected at 710 nm by using UV visible spectrophotometry (Shimadzu, UV2400PC). The ignition loss after calcination was determined as the difference of sample weight before and after calcination; 2.5 g of BPR was ignited at 100 °C to 800 °C.

Kun-tan generation and temperature changes during the charring process

We focused on the biochar making process, which was available as one of pretreatments for organic materials, as a farmer-affordable heat production technology. Low-temperature calcination of BPR has possibility to improve solubility using the heat produced by the charring of organic materials.

In the Equatorial forest zone, saw dust charring by using Kun-tan charring was preliminarily carried out. Saw dust is one of the abundant unused organic wastes produced from timber processing. The saw dust was collected from a timber mill located in Kumasi. In the Guinea savanna zone, rice husk charring was attempted. Rice husk can be used in every rice field. Rice husk was collected from a rice mill.

In this study, the equipment for Kun-tan charring was used (Figure 1; Honma Factory Co. Ltd.) as an alternative heat source. The Kun-tan was charred as follows: (1) A few wood pieces were placed inside the Kun-tan maker as ignition woods. (2) After wood pieces were ignited, the fire wood was covered by the Kun-tan maker. (3) The mixture of saw dust and BPR was set around the Kun-tan maker. (4) After white smoke was generated, a black spot would appear on the surface. (5) When the surface was charred, the samples were mixed. 6) When completely charred, the fire was

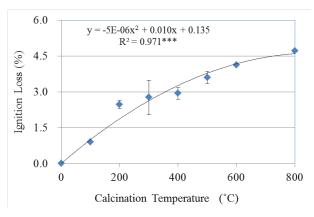**Figure 1** Kun-tan maker (Honma Factory Co. Ltd. Nigata, Japan)

extinguished by water. The charred saw dust was then dried.

The temperature changes during charring were monitored using a thermometer (CT-05SD; CUSTOM) with a high temperature sensor (LK-1200i). The sensor was placed at the center of saw dust and/or rice husk char (length, 5 cm from the Kun-tan maker; height, 5 cm from the ground surface).

RESULTS AND DISCUSSION

Ignition losses of BPR

Ignition losses of BPR with low-temperature calcination are shown in Figure 2. The ignition loses increased with temperature increase. Doak *et al*. (1965) reported that low-temperature calcination of PR, produced in New Zealand, increased the ignition losses, which reached the maximum at about 500 °C. During BPR calcination, ignition losses continued to increase up to 800 °C in this experiment. Doak *et al*. (1965) indicated that the ignition loss maximum in New Zealand PR was about 18 % at

$$y = -5E\text{-}06x^2 + 0.010x + 0.135$$
$$R^2 = 0.971^{***}$$

Figure 2 Ignition losses of BPRs with low-temperature calcination

Error bars indicate the standard error (n = 3)

500 °C, whereas BPR showed relatively lower ignition loss (4.5 %) even at 800 °C calcination.

The difference in ignition losses in two PRs seemed to suggest that various PRs have different thermal properties, reflecting the chemical and/or mineralogical composition of the PRs. New Zealand PR is guano-origin phosphate hydrate minerals which has crystallization water, such as Crandallite ($CaAl_3(PO_4)_2(OH)_5 \bullet H_2O$) and Millisite (($Na,K)CaAl_6(PO_4)4(OH)_9 \bullet 3(H_2O)$). But BPR consists of Fluorapatite without crystallization water. Thus, the effect of low-temperature calcination on PR solubilization might be different depending on the occurrence of PR, because of its chemical composition.
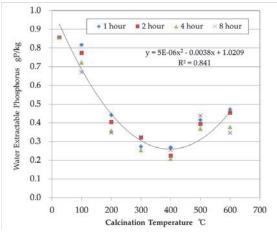
PR solubilization by using low-temperature calcination

Water-extractable P indicated the lowest value at 400 °C calcination (Figure 3). The LTC-BPR at 400 °C showed definite decrease in water solubility, i.e., 0.21 to 0.27 g P·kg^{-1} of water-extractable P, whereas BPR at room temperature contained 0.86 g P·kg^{-1} of water-extractable P.

Kimiwada *et al*. (2010) reported that the decrease of water-extractable P in poultry manure ash up to 800 °C because of low-temperature calcination. However, the increasing trend was observed over 400 °C calcination (Figure 3). The increase of water-extractable P might be attributed to the vitrification of some phosphate. However, detailed investigation will be required to determine whether vitrification occurs during low-temperature calcination.
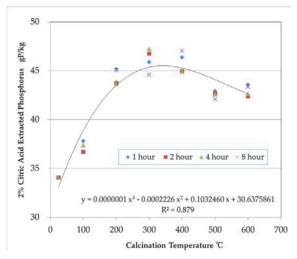
Citric acid-extractable P showed the highest value around 300 °C to 400 °C calcination, unlike water-extractable P (Figure 4). BPR at room temperature contains 34.1 g·kg^{-1} of citric acid-extractable P, and it markedly increased to 46.1 g·kg^{-1} at 300 °C and 45.8 g·kg^{-1} at 400 °C calcination. The ratio of citric acid-extractable P against total P in BPR was 22.86 % at room temperature, but LTC-BPR at 300 °C has 30.95 % and LTC-BPR at 400 °C contained 30.73 % of citric acid-extractable P against total P in BPR. In addition, citric acid-extractable P was considered as the fraction indicating the plant available P.

The largest decrease of water-extractable P was 0.59 g·kg^{-1} from un-calcined BPR, whereas the largest increase of citric acid-extractable P was 12.0 g·kg^{-1}. These results suggested that calcination around 300 °C to 400 °C can enhance the BPR solubility, especially of the citric acid-extractable fraction, whereas water solubility was slightly reduced.

Figure 3 Changes in the water solubility of BPR after low-temperature calcination.

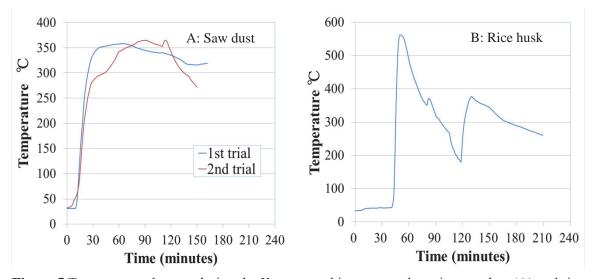**Figure 4** Changes in solubility of 2 % citric acid of the BPR by low-temperature calcination.

The time for calcination did not affect BPR solubility in both water and citric acid, suggesting that 1 h of calcination is sufficient to enhance the solubility of BPR.

The development of a farmer-applicable procedure for low-temperature calcination

As described above, if maintaining the temperature of about 350 °C for 1 h is feasible without

high cost equipment, BPR could be calcinated, remarkably improving its citric acid solubility. The time-sequential temperature changes during the process of Kun-tan making with sawdust (A) and rice husk (B) are shown in Figure 5. The temperature during saw dust charring rapidly increased at 15 min after ignition and reached 300 °C in almost 30 min (Figure 5A). The saw dust temperature was maintained 300-360 °C for about 120 min.

As can be seen from Figure 5A, saw dust charring by using the Kun-tan method can produce sufficient heat for low-temperature calcination of PR.

Figure 5 Temperature changes during the Kun-tan making process by using sawdust (A) and rice husk (B)

The time-sequential temperature changes during the rice husk charring are shown in Figure 5B. The temperature during rice husk charring rapidly increased in about 40 min after ignition and reached the maximum temperature of 560 °C. Subsequently, the temperature was maintained at about 400 °C for approximately 30 min. Then, the temperature decreased gradually until the end of charring. Unlike in the case of saw dust charring, rice husk charring did not keep the constant temperature. However, the mean temperature during rice husk charring was about 330 °C.

Low-temperature calcination with saw dust or rice husk charring are estimated to solubilize 9 to 10 % of the total P in BPR, as expected using the equation calculated from Figures 2 and 3.

Although the amount of solubilized P was extremely small for agricultural effectiveness, this technology might be improved by calcination with carbonate addition. Akiyama *et al*. (1992) showed that calcination with sodium carbonate remarkably improved the solubility of low-grade PR. Moreover, Nakamura *et al*. (2015) indicated that BPR solubility for 2 % citric acid solution can be strongly enhanced by calcination with sodium carbonate.

CONCLUSIONS

Our results suggested that improving BPR solubility by low-temperature calcination can be a potential technical option, through charring of saw dust or rice husk which are readily available organic resources for farmers in the Equatorial Forest and Guinea savanna zones. The Kun-tan method can be applied in various regions by using various crop husks or powdered organic compounds. Although low-temperature calcination enhanced the citric acid solubility of PR by 10 g P·kg⁻¹, further investigation would be required to determine the effect of low-temperature calcination with various types of carbonates on BPR solubility.

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