

Effect of Ball Milling under Various Conditions on Several Physicochemical Properties of Rock Phosphate Fertilizer

*Pengaruh Penggilingan dengan 'Ball Mill' dalam Beragam Kondisi
terhadap Beberapa Sifat Fisik-kimia Pupuk Fosfat Alam*

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ABSTRACT

A laboratory study was conducted to identify the effects of milling under various conditions, including use of water and potassium as milling lubricants, on several physicochemical properties of rock phosphate fertilizer. The identified properties were the XRD patterns, particle size distribution, surface area, and NaHCO₃-extractable P of the fertilizer. Milling for 2 hours significantly reduced particle size, promoted amorphization, increased surface area and amount of extractable P in 1N NaHCO₃ of rock phosphate fertilizer, with those effects for dry milling were much greater than for wet milling. Wet milling and use of additives (KCl and K-feldspar) minimized the occurrence of agglomeration during milling process. Although further tests in soil-plant system are required, dry milling may be recommended as a simple method for manufacturing an agronomically effective P + K fertilizer.

Keywords : *Ball mill, Rock phosphate fertilizer, Additives, K-feldspar, Agglomeration*

ABSTRAK

Percobaan di laboratorium telah dilakukan untuk mengetahui pengaruh penggilingan pada beragam kondisi, termasuk menggunakan air dan kalium sebagai pelumas, terhadap beberapa sifat fisik-kimia pupuk fosfat alam. Sifat yang diidentifikasi adalah pola XRD, sebaran ukuran partikel, luas permukaan efektif, dan jumlah P terekstrak dengan 1N NaHCO₃ dari pupuk tersebut. Penggilingan selama 2 jam telah memacu proses amorfisasi, meningkatkan luas permukaan efektif dan jumlah P terekstrak dengan 1N NaHCO₃; dan pengaruh tersebut dalam kondisi kering lebih tinggi daripada dalam kondisi basah. Penggilingan dalam kondisi basah dan penggunaan aditif (KCl dan K-feldspar) mengurangi terjadinya penggumpalan selama proses penggilingan tersebut. Meskipun pengujian lebih lanjut masih diperlukan, penggilingan dalam kondisi kering dapat direkomendasikan sebagai metode yang mudah untuk menghasilkan pupuk P + K yang secara agronomis jitu.

Kata kunci : *Ball mill (gilingan menggunakan bola baja), Pupuk fosfat alam, Bahan aditif, K-feldspar, Penggumpalan*

INTRODUCTION

The main limiting factor of using most rock fertilizers, including rock phosphate fertilizer (RPF), in agricultural practices is its slow release of P from the rock. To a certain extent, the effectiveness of RPF is determined by its particle size, while RPFs available in the market are commonly in relatively coarse particle (< 2 mm). The agronomic effectiveness of RPF may be improved by applying high-energy or ball milling. However, under which condition is that the milling will be the most beneficial, needs to be identified.

Ball milling has been used to produce super fine or nano particles of clay and minerals in ceramic industries. Many workers (Gasalla *et al.*, 1987; Kühnel and Van der Gaast, 1989; Garcia *et al.*, 1991; Sugiyama *et al.*, 1994; Aglietti, 1994; Suraj *et al.*, 1997; Uhlík *et al.*, 2000; Priyono *et al.*, 2002) have reported that the milling has major effects on several physicochemical properties of minerals and rocks. For example, Aglietti (1994) showed that dry milling of talc increased CEC and the amount of Mg dissolved in water. This method was also used to accelerate nutrient release from several silicate minerals (Harley, 2002), silicate rocks (Priyono, 2005), and rock phosphates (Lim *et al.*, 2003) in the soil, improving the agronomic effectiveness of the rock fertilizers.

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To intensive milling, however, may cause agglomeration or sintering of fine particles resulting in a decrease of the effective surface area (Priyono *et al.*, 2002) and this effect may reduce the solubility of plant nutrients from milled silicate rocks (Priyono, 2005) or RPFs (Lim *et al.*, 2002). Optimum milling condition should, therefore, be identified for each type of rock fertilizer to avoid agglomeration or sintering.

Agglomeration is due to a number of processes including exposed hydrogen ion bonding of surface hydroxyl groups on the fine particles. Agglomeration may be avoided by immersing the material in a polar liquid during milling (Veale, 1972), e.g., wet milling in H₂O (Reay, 1981; Harley 2002; Priyono *et al.*, 2002) or in hydrocarbons including alcohol (Papirer and Roland, 1981). The addition of potentially reactive additives, such as KCl and K-Na rich minerals, to eliminate agglomeration and to supply additional plant nutrient (e.g., K) may be beneficial has not been investigated for rock phosphate fertilizers.

This research was aimed to identify the effects of milling under various conditions, including use of H₂O at several rock/water ratios, KCl and K-feldspar as milling lubricants, on several physicochemical properties of RP fertilizer. The observed properties were presumed to be indicative for the agronomic effectiveness of the milled RPF.

MATERIALS AND METHODS

Sample preparation

Bulk sample of RP (composing mainly of apatite – Ca₃(PO₄)₃(F₂Cl₂OH)) was obtained from Natural Science Establishment Inc. USA, and K-feldspar was from Commercial Mineral Ltd. Perth, Western Australia (Ø < 150 µm) composing of 65.6% microcline, 31.2% albite, 0.6% anorthite, and < 2% kaolinite + free quartz . The bulk sample of RP was broken manually with a hammer to about 0.5 cm diameter and was milled using a Thema ring mill for 3 minutes and screened to pass a 250 µm screen. The initially milled RP was further milled with a ball mill (Spex 8000) using a 80 cm³ steel vial and 50 gram of Ø 5 mm steel balls for 2 hours under various conditions as summarized in Table 1.

The adhered rock powders on the mill vial were scratched with a stainless steel spatula, and for those on mill balls were removed by hand shaking the balls using stainless steel screen. All of these powders were transferred to plastic containers for storage. The wet-milled samples were removed from the mill vial and ball surfaces using a deionized water-spray bottle, and were transferred to plastic bottles through plastic panels equipped with a stainless steel screen. The suspensions of the wet-milled rocks were centrifuged for 10 minutes at

Table 1. Composition of samples loaded into milling vial and the milling conditions

No.	Sample code	Composition of sample loaded into milling vial	Milling condition
1.	RP dry	RP (Ø < 250 µm)	Dry
2.	RP W4/1	5 g RP + 1.25 ml H ₂ O	Wet (4:1)
3.	RP W1/1	5 g RP + 5 ml H ₂ O	Wet (1:1)
4.	RP W1/3	5 g RP + 15 ml H ₂ O	Wet (3:1)
5.	RP + KCl dry	4.5 g RP + 0.5 g KCl	Dry
6.	RP + KCl W4/1	4.5 g RP + 0.5 g KCl + 1.25 ml H ₂ O	Wet (4:1)
7.	RP + KCl W1/1	4.5 g RP + 0.5 g KCl + 5 ml H ₂ O	Wet (1:1)
8.	RP + KCl W1/3	4.5 g RP + 0.5 g KCl + 15 ml H ₂ O	Wet (1:3)
9.	RP + KFld dry	2.5 g RP + 2.5 g K-feldspar	Dry
10.	RP + KFld W4/1	2.5 g RP + 2.5 g K-feldspar + 1.25 ml H ₂ O	Wet (4:1)
11.	RP + KFld W1/1	2.5 g RP + 2.5 g K-feldspar + 5 ml H ₂ O	Wet (1:1)
12.	RP + KFld W1/3	2.5 g RP + 2.5 g K-feldspar + 15 ml H ₂ O	Wet (1:3)

11,000 rpm using Eppendorf 5810 Centrifuge, the supernatant was discharged and the powders were oven dried at 60° C for 48 hours.

Analytical methods

Identification for physicochemical properties of the milled rock phosphate was carried out in its original condition (without any pre-treatment) as that might be used in practices. However, an exception was made for the measurement of particle size by using Malvern Mastersizer that the rock powders were ultrasonically dispersed prior to measurement. This treatment was applied due to concern to the possibility of scratching on the detection lens of the instrument by coarse (agglomerated) particles being measured. Therefore, care should be taken in interpreting the results of this measurement as such pre-treatment to the samples may result underestimate values of particle size relative to those for the untreated RP powders.

The concentrations of major elements for the rocks initially milled and milled for 120 minutes (Table 2) were determined by XRF (Philips PW 1400) after fusing the samples with lithium metaborate (Karathanasis and Hajek, 1996). Distribution of particle size was measured in duplicate by using a Malvern Mastersizer. The

sample was ultrasonically dispersed in water for 5 minutes prior to measurement and stirred continuously during measurement. Specific surface area of duplicate samples (without dispersion) was measured by the BET-N₂ method using a Micromeritics Gemini III 2385 Surface Area Analyser. Mineralogical characteristics of rock powders were derived through analysis of XRD patterns by applying a X-ray Powder Diffraction Analysis Software (XPAS) V.3.0 described by Singh and Gilkes (1992). The values of relative peak height (RePH) and relative peak width at half peak (RePWHP) of milled RP under various conditions over those for initially milled rock were measured using this method for the mineral faces (hkl) of 002 and 202 (d-spacing = 3.44 and 2.62 Å, respectively), representing all XRD peaks of RP. The XRD patterns of rock powder were collected with a Philips PW-3020 diffractometer using monochromatised Cu K α radiation, generated at 50 kV and 20 mA. The diffraction intensity was recorded between 5 and 70° 2 θ angles at a scanning rate of 0.02° per second.

The quantity of soluble P for the milled RP was determined using 1N NaHCO₃ as an extracting solution. Rock powder (2.5 g) was added to 50 ml of the extracting solution in a 100 ml plastic bottle, shaken for 2 hours on an end-over-end shaker. The

Table 2. Composition of total main elements¹ in rock phosphate milled for 2 hours under various conditions

No.	Milling condition/sample code	Element							
		Fe ₂ O ₃	CaO	K ₂ O	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O
..... % oxides									
1.	Initially milled RP	0.31	36.97	0.41	32.65	20.01	6.69	1.72	0.77
2.	RP dry	0.36	37.14	0.41	31.68	20.34	6.94	1.79	0.70
3.	RP W4/1	2.42	39.72	1.08	24.77	21.06	6.97	1.96	1.56
4.	RP W1/1	2.56	39.93	0.41	24.90	21.37	7.15	2.05	1.19
5.	RP W1/3	1.76	40.35	0.41	25.17	21.34	7.05	1.96	1.11
6.	RP + KCl dry	0.56	36.36	6.68	23.55	21.41	7.21	2.18	1.52
7.	RP + KCl W4/1	1.90	40.63	0.40	25.23	21.43	6.95	1.99	1.05
8.	RP + KCl W1/1	3.13	39.70	1.17	25.79	20.64	6.71	1.89	0.86
9.	RP + KCl W1/3	2.45	39.35	1.22	25.60	21.16	6.96	1.92	0.91
10.	RP + KFlid dry	0.23	20.29	5.59	12.70	44.44	13.39	1.29	2.01
11.	RP + KFlid W4/1	3.09	20.44	5.43	12.53	42.39	12.61	1.37	1.66
12.	RP + KFlid W1/1	2.47	20.31	5.49	12.15	42.69	12.91	1.48	2.59
13.	RP + KFlid W1/3	3.52	20.64	5.54	12.67	41.85	12.49	1.17	1.80

¹ Concentrations of SO₃, MnO, TiO₂ were less than 0.5%

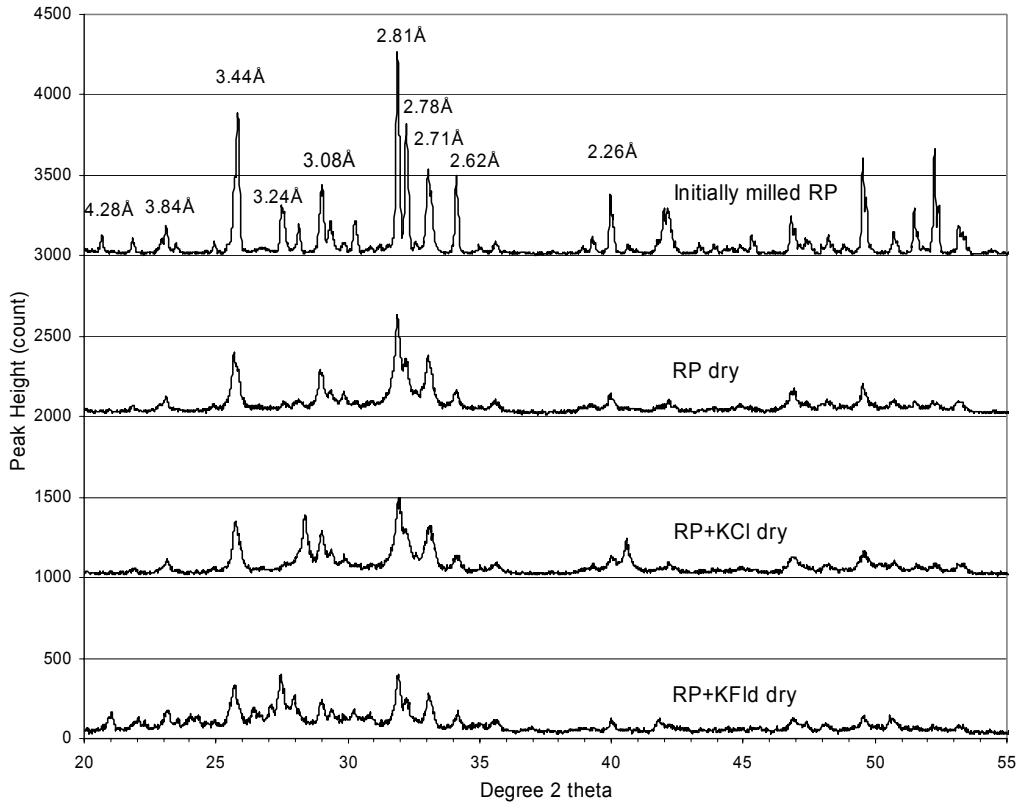


Figure 1. The XRD pattern of initially milled ($\varnothing < 250 \mu\text{m}$) and dry milled rock phosphates for 120 minutes; and mineral faces (hkl) of 002 and 202 (d-spacing of 3.44 and 2.62 Å respectively) as shown. The zero value of peak height for each milled RP is at grid line just under its XRD

suspension was centrifuged for 20 minutes at speed of 11,000 rpm, and the concentration of P in the filtrates was determined by spectrophotometer after blue complexation with a molibdat-stano chloride reagent.

RESULTS AND DISCUSSION

Characteristics of XRD patterns

The XRD patterns of initially milled RP, RP dry, RP + KCl dry, and RP + KFId dry are presented in Figure 1 as an example, and the RePH and RePWHP of representative XRD peaks for the powder milled under each milling condition relative to those for the initially milled RP are presented in Table 3.

Milling for 2 hours under any milling condition greatly reduced XRD intensity ($\text{RePH} < 100\%$) and enlarged peak width at half peak ($\text{RePWHP} > 100\%$) (Table 3). These trends indicate that milling reduced crystal size and induced structural disorder of the minerals which decreased total diffracted intensity (i.e., area under peak) as amorphous material does not diffract coherently but contributes to background scattering. The increased broadening of XRD reflections indicates a reduction in the crystal size of the remaining crystalline mineral (Klug and Alexander, 1974).

Comparisons for the RePH and RePWHP values were made. The RePH values for dry milled RP were slightly lower than those for wet milled RP. Inversely, the RePWHP values for dry milled RP were higher than those for wet milled RP. These

Table 3. Mean values of relative peak height (REPH) and relative peak width at half peak (REPWHP) of milled rock phosphate under various conditions over those for initially milled rock

No.	Milled condition/sample code	REPH	REPWHP
	 %	
1.	Initially milled RP	100	100
2.	RP dry	38	229
3.	RP W4/1	49	157
4.	RP W1/1	40	201
5.	RP W1/3	55	145
6.	RP + KCl dry	35	269
7.	RP + KCl W4/1	33	201
8.	RP + KCl W1/1	40	175
9.	RP + KCl W1/3	44	153
10.	RP + KFId dry	37	244
11.	RP + KFId W4/1	40	200
12.	RP + KFId W1/1	34	245
13.	RP + KFId W1/3	45	194

Table 4. Median particle size (D_{50}), surface area (SA), and 1N NaHCO_3 -extractable P_2O_5 for rock phosphate milled for 2 hours under dry and wet conditions at rock/water ratios of 4/1, 1/1, 1/3 (W4/1, W1/1, W1/3); + KCl and + K-feldspar

No.	Milled condition/sample code	D_{50}	SA	Extractable P_2O_5
		μm	$\text{m}^2 \text{g}^{-1}$	% to total in PR
1.	Initially milled RP	61.70	1.03	0.10
2.	RP dry	2.71	3.97	9.73
3.	RP W4/1	1.44	34.72	0.66
4.	RP W1/1	1.79	43.53	0.79
5.	RP W1/3	2.50	29.16	0.80
6.	RP + KCl dry	2.30	5.75	6.46
7.	RP + KCl W4/1	1.89	31.35	2.24
8.	RP + KCl W1/1	3.84	50.74	0.58
9.	RP + KCl W1/3	2.01	36.72	0.54
10.	RP + KFId dry	2.48	5.26	21.17
11.	RP + KFId W4/1	3.44	33.47	1.15
12.	RP + KFId W1/1	3.28	31.74	1.38
13.	RP + KFId W1/3	3.38	22.47	0.99

trends indicate that amorphization due to dry milling was greater than that due to wet milling, and the trends were similar to those found by Priyono and Gilkes (2004) for ball milled silicate rocks. Whether this amorphization is followed by the improvement of quantity of P released from RPF in soil-plant system, as does for that of Ca, Mg, and K from ball milled silicate rocks (Priyono and Gilkes, 2004), however, can not be interpreted based on these present data due to differences in chemical reactions of these plant-nutrient elements in rhyzosfer.

Particle size, surface area, and quantity of soluble P

Data of median particle size (D_{50}), means surface area, and quantity of extractable P are presented in Table 4. For all applied conditions in this present experiment, milling for 2 hours reduced particle size of RP up to 20 - 30 fold finer than that for initially milled RP with the greatest effects was for milling under wet condition at a rock/water ratio of 4/1 (RP W 4/1). For the milled RP without additives, this reduction of particle size was followed by the increase of surface area, but there

was no systematic trend of that for RP + KCl and RP + KfId.

As shown in Table 4, there was little effect of adding KCl or K-feldspar as dry milling lubricants to particle size of milling product (e.g., RP dry vs RP + KCl dry and RP + KfId dry = 2.71 vs 2.30, and 2.48 μm). However, dry milling for 2 hours, with or without additives, increased surface area for 2-5 fold (see values of SA at row 1 vs those at rows 2, 6, and 10 in Table 4), while this effect for wet milling was much larger (e.g., about 30-50 fold) relative to that for initially milled RP (see the SA values at row 1 vs those at rows 3 to 5, 7 to 9, and 11 to 13 in Table 4).

Agglomeration of dry-milled silicate minerals has been reported for α -spodumene (Gasalla *et al.*, 1987), kaolins (Juhász, 1980; Garcia *et al.*, 1991), talc (Aglietti, 1994), antigorite (Drief and Neito, 1999), and four types of silicate rocks (Priyono, 2005). These authors reported that different grinding times were necessary for the occurrence of agglomeration depending on milling procedure and mineral species, and that agglomeration either decreased surface area (Garcia *et al.*, 1991; Sánchez-Soto *et al.*, 1997; Priyono, 2005) or increased surface area (Gasalla *et al.*, 1987). Results of the present research indicate that agglomeration occurred during dry milling, but did not to little in wet milling.

As shown in Table 4, the decreases in particle size or increases in surface area due to milling did not systematically associate to the increases in amount of dissolvable P_2O_5 of milling products in the extracting solution (NaHCO_3). Dry milling that promoted amorphism caused smaller increases of surface area but larger increases of the amount of P extractable with NaHCO_3 than those for wet milling (see those values at rows 2, 6, and 10 respectively vs those at rows 3 to 5, 7 to 9, and 11 to 13 in Table 4). However, care should be taken in interpreting this result because some of soluble P for wet milling were discharged during sample

preparation reducing the total amount of P relative to that for initially milled RP (see Table 3). If the values of total P for wet milled rocks were set to be equal to those for initially milled rock, and P in the discharged filtrate were added to the measured amount of soluble P for wet milled rocks, the results would be as follows:

1. For milling without adding additives: the amounts of soluble P for wet milled RP without lubricant would be double than that for dry milled RP.
2. For milling with adding KCl or K-feldspar: the amounts of soluble P for dry milled RP would be about 10-20% (of total in RP) which were larger than those for wet milled RP.
3. Adding KCl or K-feldspar as milling lubricant will increase soluble P by about 10 and 5% (of total P in RP) respectively for dry and wet millings.

Clearly, wet milling and use of K-feldspar additive minimized the occurrence of agglomeration thus increased soluble P from the milled RP, while this effect for added KCl was less than that for added K-feldspar. For wet milled RP, however, most soluble P was loss during milling process. In addition, wet milling requiring drying processes will be impractical in manufacturing RP fertilizer. Therefore, dry milling of RP mixed with K-feldspar may be recommended as this milling method greatly improved soluble P and enriched the RP fertilizer with K.

CONCLUSION

Ball milling for 2 hours increased surface area, and promoted amorphism of RP, with those effects were greater for dry milling than for wet milling. The changes of physical properties (particle size and surface area) due to milling did not closely correlate to the increases in soluble P of the milled RP due to the occurrence of agglomeration for dry milled RP

limiting the release of P. Agglomeration could be minimized by adding H₂O, KCl, or K-feldspar during milling process. Dry milling of RP mixed with K-feldspar may be recommended as a simple method for manufacturing an effective P + K fertilizer. The true agronomic effectiveness of the recommended milling method and condition, however, requires further evaluations in various soil-plant systems.

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