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Mechanical Grinding Improved Quality of Potassium-feldspar Rocks

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Abstract. Potassium-feldspar rocks were ground for 10, 40, 120 and 180 minutes respectively using a porcelain ball mill. The kinetics of potassium release from activated rocks and their effect on yield and nutrient uptake by grain amaranth were evaluated. Results showed that high intensive grinding could improve physicochemical properties and bioavailability of potassium-feldspar rocks. With increasing grinding time, the particle diameters were decreased, the specific surface areas were increased, and the diffraction peaks were decreased remarkably. Maximum release of acid-soluble K was obtained in all rocks during the initial stages of leaching (0-10days), but their differences narrowed down at latter stages (10-60days). The cumulative release of K from the rock treated for 180 minutes was the highest amount (5331.51 K mg/kg rocks) and was 3.75, 1.29 and 19.8% higher than the rocks treated for 10, 40 and 120 minutes, respectively. Data from pot experiment revealed that activated rocks with higher bioavailability promoted the growth and K accumulation of gain amaranth. This study indicated that mechanical activation could be an alternate technology for the efficient of using potassium-feldspar rocks for crop production.

Introduction

Application of the potassium-feldspar rocks have positively affected soil properties and stimulated plant growth [1-4]. However, compared to the conventional potassium fertilizers, crushed or ground potassium-feldspar rocks exhibit a much slower potassium release [5-6]and the effectiveness is relatively lower and a large amount of materials have to be applied to meet crop needs [7]. It is necessary to find the way to accelerate the nutrients release from the potassium-feldspar rocks to soil solution. One of the potential methods is to mobilize structural K through mechanical activation with high intensive grinding [8-10]. The objective of this investigation was to determine 1) effects of mechanical activation on physical properties in potassium-feldspar rocks, 2) the release kinetics of K from the activated rocks treated at different times, and 3) effect of activated rocks on yield and uptake of K by grain amaranth.

Experimental

Materials. The original rock applied in this research was potassium-feldspar mineral from Yuexi of Anhui province in P. R. China. The rock was ground to, about 0.5-0.8 cm. According to the determination of X-ray diffraction, the main peak of the sample's pattern identified the potassium-feldspar [$KAlSi_3O_8$]. Where the main component contained a 67.8% of SiO_2, a 17.6% of

Al_2O_3 and 10.7% of K_2O, and small amounts of Na_2O and P_2O_5 were identified using a HK-2000 Inductively Coupled Plasma Optical Emission Spectrometer. The representative samples of the potassium-feldspar rocks were activated by using a porcelain ball mill (WJH-1). The porcelain ball mill had a Φ800 mm × 1200 mm bowl with 0.75 tone stainless steel balls and a diameter of 10 mm. The bowl was filled with 30 kg of original potassium-feldspar rocks; rotational speed was set to 36 rpm; grinding time was set to 10 minutes, 40 minutes, 120 minutes and 180 minutes. The relevant parameters of the different samples were shown in Table 1.

Table 1 Physical characteristics of activated potassium-feldspar rocks.

Treat.	Time (min.)	Size distribution [μm]		Specific Surface Area [m^2/g]
		D50	D97	
T0	10	9.55	42.51	0.67
T1	40	6.58	31.95	1.07
T2	120	3.65	18.15	1.49
T3	180	3.12	12.06	1.64

Leaching experiment. The leaching experiments were performed as batch cascade test in which the solid material was subjected to sixty successive leaching steps. The test was conducted using a number of 50 ml acid-washed high-density polyethylene bottles by exposing individual 2.000 g samples of the different treatments to 20 ml of a solution consisting of 0.01 mol/L HNO3. During each leaching step, the resulting suspensions were conditioned by a standstill at 25.0 ± 0.1℃, using a thermostatic incubator. Following the first leaching step, each suspension was centrifuged at approximately 4500 g for 10 min before the supernatant was gently decanted. The second leaching step was then initiated by adding 20 ml of fresh solution to the remaining solid phase and losening the remaining solid phase by a high-strength rod. The procedure was repeated to and continued till the final step. Each of sixty successive leaching steps lasted 24 h. The filtrates were analyzed using a 6400A flame photometer.

The data which generated from the leaching experiment was fitted into the parabolic and linear empirical equations, respectively [11] and rate of K release from activated rocks were computed as:

$$Q_t = Q_o + k_p t^{1/2} \tag{1}$$

and

$$Q_t = Q_o + k_1 t \tag{2}$$

where Q_t (mg/kg) is the mass transfer of K^+ into solution at time t (days), Q_o (mg/kg) is the result of extrapolation of either Eqn.1 or 2 to time zero and is a function of initial surface ion exchange [12], and k_p (mg/(kg·d$^{1/2}$)) and k_l (mg/(kg·d)) are the parabolic and liner rate coefficients, respectively.

Pot culture experiment. Each pot contained a mixture of 350 g (20-80 mesh) quartz sand and 17.5 g rocks. Six treatments were set up, comprising the four activated rocks, quartz with enough K in nutrient solution, and quartz without K. Seeds of grain amaranth (R104) were treated in hot water for 15 minutes, germinated at 25℃ for 3 days, cultivated in the pots at a density of three plants/pot with three replicates of each. In the first week, pots were watered with distilled water for 3 days, then 50 ml of nutrient solution [13] without K was added to each pot every day, while a nutrient solution containing K was only added to the quartz with full K treatment. The pH of all solutions was adjusted to a pH 6.5 with 0.01 mol/L HCl or 0.01 mol/L NaOH. The pots were placed in a growth chamber with a daily temperature of 24-28℃, and 16 h of light for 60 days. At the end of the experiments, the above-ground part of the plants was harvested for analysis. Plant samples were dried firstly at 100 ℃ for 20 minutes, then at 65 ℃ for 72 h. The oven-dried sample were weighed, milled and digested using the H_2SO_4 + H_2O_2 method [14] for K concentration determination with a flame spectrophotometer.

Characterization. The overall chemical composition of the potassium-feldspar rock with respect to major elements was determined using inductively coupled plasma optical emission spectrometer methods (ICP-OES) using a HK-2000 Inductively Coupled Plasma Optical Emission Spectrometer. The potassium-feldspar rocks were subjected to an X-ray powder diffraction analysis (XRD) to identify the crystal structure and the current phases, using a RINT-2000 diffractometer with Cu Kα radiation and scanning velocity was 2°/min in the ring of 20-50°. The size distributions of the activated potassium-feldspar rocks were determined by BT-9300H Laser particle size analyzer, and the specific surface area was determined using the N_2-adsorption technique and a Flow SBT-127 volumetric gas adsorption analyzer. Scanning electron microscopy (SEM) measurements were performed on a JSM-6301F microscope.

Results and Discussion

Effects of grinding on physical properties of potassium-feldspar. Table 1 showed that the particle size and specific surface area (SSA) of the rocks changed as a function of grinding time. The particle size significantly decreased when the grinding time was prolonged. The size reduction particle of the ground rocks appeared to prevail from 10 minutes to 120 minutes. Subsequently, the particle size declined slowly. The minimum particle size was attained at 180 minutes (T3 rock), and the value of D97 and D50 were reduced by 67.33% and 71.63% than T0 rock, respectively. More fine particles led to a rapid increase of the SSA of the potassium-feldspar. The SSA of T3 rock was higher by 1.44, 53.27% and 10.07% than T0 rock, T1 rock and T2 rock, respectively. This indicated that a reduction in the particle size down to 1.64 m^2/g was simply attained and the increased fine particle could be caused by prolonged grinding due to mechanical fracturing.

Figure 1 showed that the surface morphology of potassium-feldspar rocks, activated by a porcelain ball mill, changed with time. The potassium-feldspar grains had an irregular and angular particle shape in the early stages of grinding (T0 rock). The practical aspects of mechano-activation alterations caused overall structural modifications of potassium-feldspar rock when grinding beyond approximately 10 minutes. The rock particle broke down to finer particles and the potassium-feldspar structure altered gradually and the number of void space was increased. Especially, in Figure 1-T3 rock, the surface of particles was rough and the structure of particles was loose. Combining these photomicrographs with the results of SSA of the ground rocks ranging from 10 to 180 minutes suggested that SSA could increase due to mechanical fracturing of the potassium-feldspar.

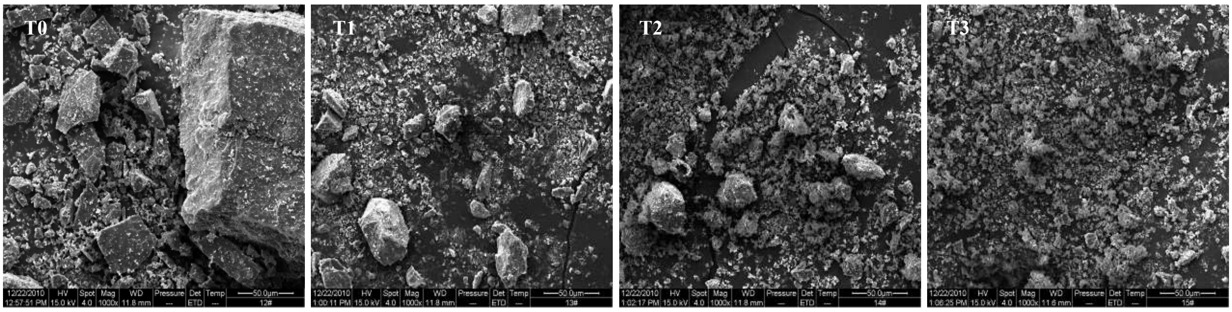

Figure 1 Scanning electron micrographs of activated potassium-feldspar rocks: T0-10min, T1-40min, T2-120min and T3-180min

Figure 2 showed the X-ray diffraction patterns of potassium-feldspar rocks under the treatment of different times. The main peaks of potassium-feldspar tended to reduce their intensity as the grinding progresses in time. According to the XRD patterns, the amorphization attained of potassium-feldspar was attributed to disordering in their structure by action of external forces. Thus, the distortion induced by grinding was reflected in the peak width broadening when the intensity of the peak was decreased. The change of mean lattice strain was determined for the individual (h k l) reflections of the potassium-feldspar. Then the (0 4 0), (0 6 0) and (2 0 1) lattice planes in short grinding times undergo a remarkable change and they become amorphous. These patterns revealed that the structure changed for mechanical activation of potassium-feldspar by the energy-intensity porcelain ball mill.

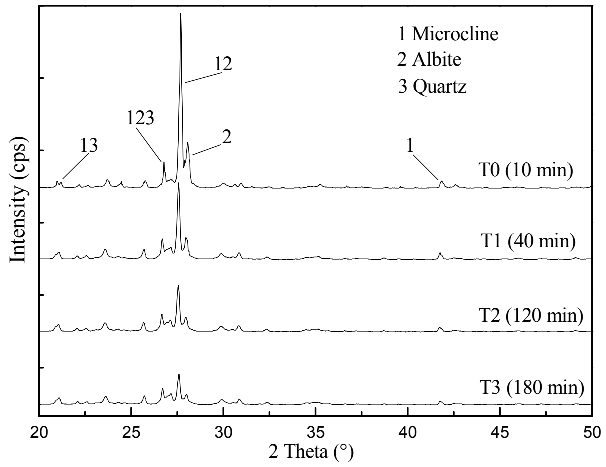

Figure 2 X-ray diffraction pattern of potassium-feldspar at progressive grinding time.

Effects of grinding on K release of potassium-feldspar. A perusal of the data (Figure 3-a) showed significantly higher amount of K release from various potassium-feldspar rocks during the initial stages of leaching. It declined sharply up to 10th day of leaching, thereafter decreased steadily up to 60th day of leaching. Among the various potassium-feldspar rocks, in the first stage of leaching (10th day), T3 rock had the highest K release (1432.69 K mg/kg rocks), followed by T2 rock (1148.21 K mg/kg rocks), T1 rock (667.17 K mg/kg rocks) and least with T0 rock (247.18 K mg/kg rocks). From the second leaching onwards (10th day), the differences among the different rocks narrowed down. At the end of the leaching (60th day), T3 rock had a higher K release by 3.52, 1.40 and 16.62% than T0 rock, T1 rock and T2 rock, respectively. This indicated that a higher K release from potassium-feldspar rocks could be caused by prolonged grinding due to mechanical fracturing.

The cumulative release of acid-soluble K (ASK) from various potassium-feldspar rocks (Figure 3-b) was computed from the amount of ASK released at different periods of leaching. It was the sum of all the amount of K released (K mg/kg rocks) at a particular time. The cumulative release of ASK was plotted against period of leaching (days). It was evident that cumulative release of ASK showed an increasing trend. The rate of increase was significantly higher in the initial stages of leaching (up to 10th day), thereafter it increased at a diminishing rate up to 60th day. Among the rocks, the maximum cumulative release of ASK was obtained in T3 rock (5331.51 K mg/kg rocks) treated for 180 minutes, closely followed by T2 rock (4450.04 K mg/kg rocks), then by T1 rock (2331.77 K mg/kg rocks) and least with T0 rock (1121.62 K mg/kg rocks). It was also evident that activated rocks prepared with more time had a higher cumulative K release throughout the leaching period.

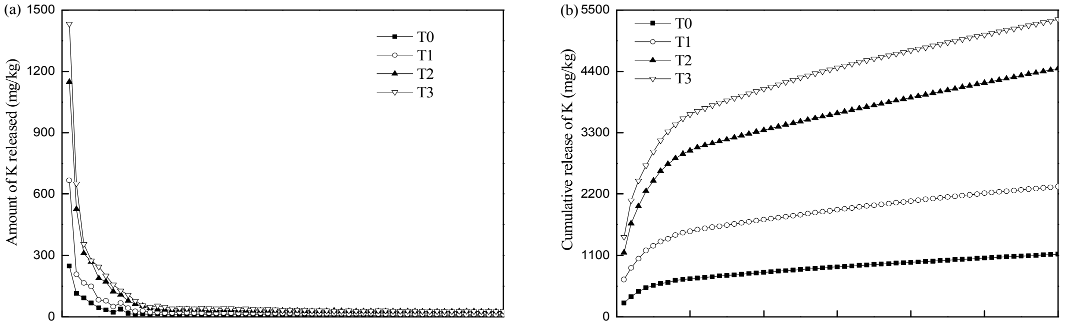

Figure 3 Release pattern of acid-soluble K from various potassium-feldspar rocks during different periods of leaching: (a) the single K release and (b) the cumulative K release.

Data revealed that the release rates of K from the rocks in the acid solution followed a two stage process (Table 2). The first stage was characterized by a nonlinear release of K and was best described by the parabolic rate equation (Eqn. 1). In the second stage, the release of K was linear with time. The first stage occurred up to 10th day, followed by linear release until the termination of the experiment (60th day). Calculated rate coefficients for both stages in the experiment showed similar trends with rate constants for the release of K decreasing in the order T3 rock > T2 rock > T1 rock > T0 rock. This indicated the quantity of dissolved K from potassium-feldspar rocks increased with grinding time due to mechanical fracturing.

Table 2 The values of kinetics parameters for K dissolution from the rocks.

Treat.	Time [min.]	Q_o [mg/kg]	k_p [mg/(kg·$d^{1/2}$)]	k_l [mg/(kg·d)]	R^2
Parabolic release (0-10 days)					
T0	10	89.67	198.10	-	0.96
T1	40	324.36	402.55	-	0.98
T2	120	482.97	834.70	-	0.97
T3	180	641.41	993.45	-	0.97
Linear release (10-60 days)					
T0	10	621.14	-	8.66	0.99
T1	40	1423.67	-	15.80	0.99
T2	120	2765.82	-	28.65	1.00
T3	180	3422.62	-	32.94	0.99

Effects of grinding on bioavailability of potassium-feldspar. As indicated by the dry matter accumulation (Figure 4-a), additions of full nutrient solution or activated potassium-feldspar rocks resulted in significantly higher dry matter than the quartz treatment. Among the K supply treatments, the highest dry matter (3.39 g/pot) accumulation was in full-K treatment with nutrient solution. Potassium supply by different activated potassium-feldspar rocks increased the growth of grain amaranth and the growth was substantially higher with increasing grinding time. Treatment T3, with rocks activated for 180 minutes, had significantly higher dry matter (3.00 g/pot) than others. This showed that activated potassium-feldspar rocks could help in higher dry matter of grain amaranth.

Application of full nutrient solution and activated potassium-feldspar rocks also resulted in significantly higher K uptake by grain amaranth than the Quartz treatment (Figure 4-b). Significantly higher K uptake by grain amaranth (146.02 mg/pot) was recorded in Full K treatment compared to other treatments. The higher K uptake in Full K treatment was due to presence of higher amount of water-soluble K in it. Among the activated potassium-feldspar rocks, the order of K uptake was consistent with the dry matter of grain amaranth and Treatment T3 had significantly higher K uptake (109.16 mg/pot) than others. This indicated that a higher bioavailability of activated potassium-feldspar rocks could be caused by prolonged grinding due to mechanical fracturing.

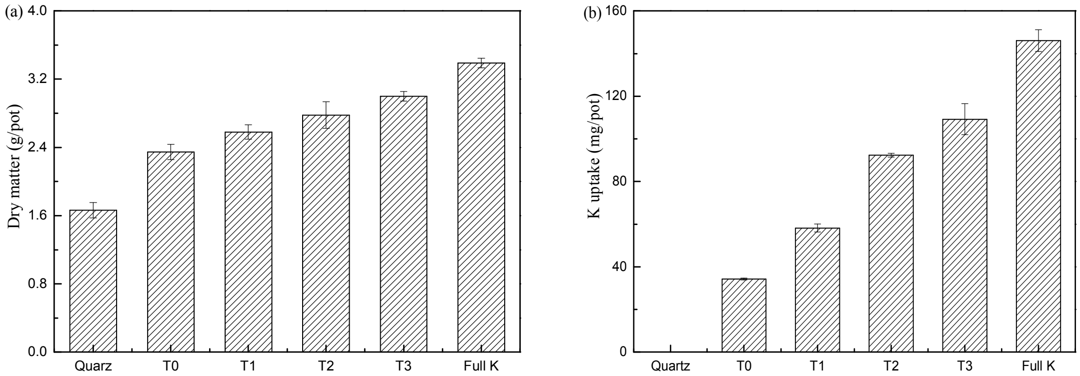

Figure 4 Dry matter accumulation (a) and potassium uptake (b) of grain amaranth with different K supplied.

Conclusions

The results of this study showed that potassium-feldspar, when activated by a porcelain ball mill for a certain time, could significantly reduce particle size, increase specific surface area and abundance of amorphous and disordered constituents. These changes also resulted in an increase in the proportion of readily soluble K from the rock and the amount of reactive sites on the surface of particles. Furthermore, the activated potassium-feldspar rocks might provide a considerable portion of K required for plant growth. Therefore, mechanical activation could be an alternate technology for the efficient of using potassium-feldspar rocks in crop production, which could help to reduce the reliance on costly chemical fertilizers.

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