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Environment-Friendly Synthesis of Feldspar-KH_2PO_4 Complexes by Mechanochemical Reaction

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Abstract. Novel materials from Feldspar as clay material and KH_2PO_4 (KHP) are prepared by grinding in a planetary ball mill in a mechanochemical process, one of the most effective ways to synthesize slow-release fertilizers. In two paths, tests were carried out with (3) weight ratio of Feldspar: KH_2PO_4 contents, at mill The incorporation of KH_2PO_4 and the liberation of K+ and $PO_4{}^{3-}$ ions into solution were assessed at rotating speeds ranging from 200 to 700 rpm for two hours, and at milling periods ranging from 1 h, 2 h, and 3 h. Thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and ion chromatography (IC) were employed to analyze the produced materials. The results confirmed that the mechanochemistry process is a sustainable chemistry method to produce amorphous Feldspars containing KH_2PO_4. After dispersing Feldspar and KH_2PO_4 in water for 24 h, K^+ and $PO_4{}^{3-}$ ions were measured. Based on these studies, it has been demonstrated that intercalated Feldspar could function as a carrier of K^+ ions and release PO_4^{3-} ions as a slow fertilizer.

Keywords: Mechanochemical, Intelligent Fertilizers, Efficiency, Nutrients, Ball milling, Slow-release, Feldspar.

INTRODUCTION

As global food consumption continues to rise in the coming years. Global food demand will increase approximately 60% by 2050 compared to 2005, according to the United Nations' Food and Agriculture Organization [19]. Crop production has to be increased in agriculture to fulfill global food demand. One of the most efficient ways to spur plant growth is fertilizer, which can play a significant role in increasing crop productivity [5]. Environmental pollution is caused by fertilizer use, which results in health problems. Several factors contribute to environmental pollution, including the high solubility of nutrients and their leaching followed by soil mobility [12].

Plants can only use a small number of chemical fertilizers because they are highly soluble in water. Several processes affect the rest of them when they are applied to a field, such as adsorption, degradation, runoff, and leaching. In other words, soluble chemical fertilizers are quite ineffective. Because fertilizers are derived from inorganic anions such as nitrate and phosphate, excessive application of fertilizers can cause contamination of surface water and soil [13].

There have been several types of slow-release fertilizers made from different materials, including various minerals [3, 8, 9, 23]. Slow-release mineral fertilizers have gained a lot of attention for their environment-friendly properties and ability to maintain soil fertility. Minerals are usually charged to protect nutrients from rapid degradation as well as having a crystal structure [1, 6, 14, 18, 21, 23].

The mineral feldspar is the most common one found in rocks. A group of minerals that are known collectively as feldspar is a mineral with the chemical formula x Al (Al, Si)$_3$O$_8$, where x might be calcium (Ca), sodium (Na), or potassium (K). Because of their high alumina and alkali contents, feldspars are predominantly utilized in industrial applications [4]. Feldspar is used to describe a wide range of materials. We use feldspar in a substantial number of everyday products, including drinking glasses, windshields, fiberglass for insulation, bathroom floor tiles, shower basins, and even the dishes on our tables. Feldspar is ubiquitous. An infinite number of tetrahedral SiO_2

and AlO_4 networks comprise the crystal structure of feldspars [4].

According to Zhang et al. [22], the minerals that contain at least some albite or anorthite are called plagioclase feldspars. In contrast, those that include alkali feldspars are known as orthoclase feldspars [16]. Due to feldspars' industrial application, the latter category is especially interesting. Depending on the type of alkali they contain, feldspars can also be divided into sodium, potassium, and mixed types [22]. Thermal gravimetric analysis (TGA), Fourier transforms Infrared (FT-IR), and x-ray diffraction (XRD) were used to explain the unique properties of Feldspar [20].

There is a wide range of applications for feldspars, from fluxing agents for ceramics to fillers for paint, rubber, and adhesive industry purposes [4, 15]. Therefore, this research aims to optimize control/slow-release fertilizers (C/SRFs) by combining feldspar minerals with KH_2PO_4 fertilizers using a dry mechanochemical approach. We aim to highlight the significance of adjusting the milling time and rotation speed in the synthesis of feldspar slow-release fertilizers by studying their mechanochemical properties.

EXPERIMENTAL SECTIONS

Mechanochemical Processes and Materials

High-purity feldspar from the Yutum Granite Suite ($KAlSi_3O_8$) (part of the Aqaba complex) [2, 4] and Panreac, PRS undergoes mechanical reactions with potassium dihydrogen phosphate (KH_2PO_4). Ball mill, planetary (Pulverisette-7, Fritsch, Germany), was used for milling under a choice of time and rotation speed, using 6.0 g (3:1) feldspar/fertilizer and 7 steel balls of 15 mm diameter. In each experiment, alternating 10 min of milling with 5 min of rest was done to prevent excessive heat from accumulating during milling. Two discussed parameters were studied as follows:

Table 1. Experimental conditions and mix ratios are listed.

Series	Sample (Feldspar: KH_2PO_4) Ratio of Weight	Rotational Speed (rpm)	Time (min)
Exp. 1	3:1	100, 200, 400, 600	120
Exp. 2	3:1	600	60, 120, 180

Characterization

X-ray diffraction measurements were performed on the Feldspar–KH_2PO_4 samples before and after milling. Radiation was Cu K has a range of 2° between 5° and 90°. The produced samples were examined using infrared spectrometers as the NEXUS and the EPS-870. At a resolution of 2 cm^{-1}, the sensors were scanned from 4,000 to 500 cm^{-1} an advanced sensor (not KBr). Using a NETZSCH STAT-409 PC thermal gravimetric analyzer in an N_2 atmosphere, the analysis was performed in 10°C/min increments from room temperature to 1,000°C.

A 100-ml glass beaker was used to conduct the leaching tests with KH_2PO_4 ground in distilled water. The parameters were the following: 1.0 g of ground sample, 20 ml of distilled water, and 24 h of incubation. Vacuum filtration with 0.45 μm pore size filter paper was used after leaching to separate solids from liquids. The parameters of the liquid ion chromatography were determined by the concentration of the K^+, $NH_4{}^+$, and PO_4^{3-} ions (nutrients) in the filtrate along with determining the total nitrogen released from urea by the Kjeldahl Nitrogen Determination instrument (IC, Thermo Scientific, column series Dionex, CS-5000+DP, Germany).

RESULTS AND DISCUSSION

Hae-Jin Jung, Md Abdul Malek, JiYeon Ryu, BoWha Kim, Young-Chul Song, HyeKyeong Kim, and Chul-Un Ro.

There are no studies available providing data on slow-release fertilizer systems synthesized from feldspar and fertilizers. More research is needed on the effectiveness of different parameters in fertilization. During amorphous material developed and reacted with salts during the production of feldspar, changing the solubility profile of compounds and generating new interactions. It has been established that feldspar has a neutral, layered alkaline structure that does not interact with other substances, including the study's target phosphate salts.

Feldspar–KH_2PO_4 System

We investigated the influence of the milling speed and the milling time in the high-energy ball mill. To achieve the most suitable conditions for utilizing the slow-release properties of nutrients, a series of experiments were conducted with feldspar and selected fertilizers.

Mechanochemical synthesis of Feldspar-KH_2PO_4 as SRF – effect of milling speed

In this study, the phosphate salts of interest were studied as amorphous feldspars produced by the formation of polymorphous aggregates. The emergence of amorphous materials changed the solubility profiles of the salts and enhanced interactions between the products that were obtained. As shown in Figure 1, amorphization of the Feldspar–KH_2PO_4 (3:1 weight ratio) sample mixture is influenced by mill rotational speed. The mill rotational speed ranged between 100 and 600 rpm for all experimental runs, with a fixed milling time of 120 min. When mill rotation speeds between 100 and 400 rpm were lowered, characteristic patterns related to KH_2PO_4 were still visible in the milled products. The higher mill speeds yielded a complete amorphous reduction of the samples, which

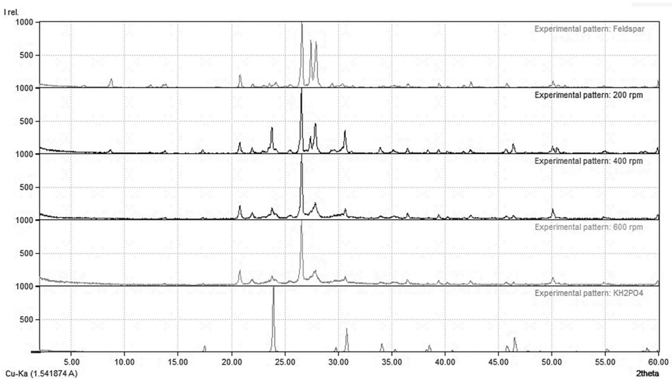

Figure 1. An XRD pattern of the Feldspar–KH_2PO_4 sample mixture was milled at varying mill rotational speeds for 120 min.

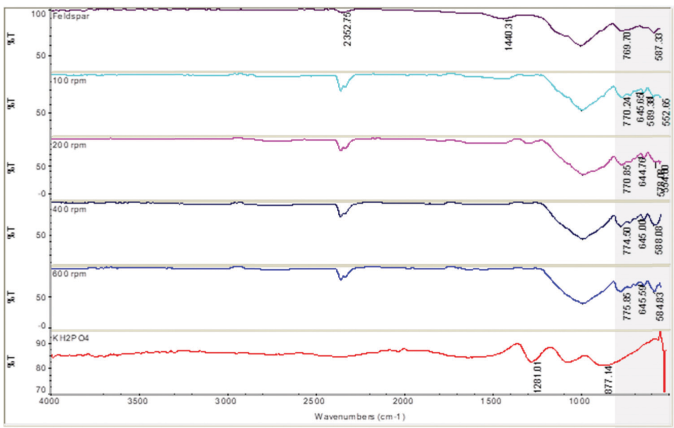

Figure 2. FTIR spectra of samples Feldspar–KH_2PO_4 milled at varied rotating speeds for 2 h.

suggests the amorphous structure of feldspar incorporates KH_2PO_4.

Each of the experimental runs was run for 120 min with mill rotation speeds ranging from 100 to 600 rpm for the FT-IR spectra to be collected. The characteristic spectrums of KH_2PO_4 at 1,281 cm^{-1} remained in the milled products at lower mill rotational speeds, such as 100–400 rpm, as shown in Fig. 2. As a result, the clear band at 1,281 cm^{-1} on the KH_2PO_4 spectrum was eliminated from sample mixtures that were milled at speeds of 400 rpm, which suggests successful intercalation of KH_2PO_4 in feldspar, distinctive due to the overlap of Al-OH, Si-O, and P-O vibrations, wide bands were seen in the area approximately 1,000 cm^{-1} for all samples [7, 10, 17].

Moreover, the shoulder band of feldspar at (1,100 cm^{-1}) vanished when milling over 400 rpm, which indicates a better mechanochemical reaction, occurs at high milling speeds than at low speeds. The thermal gravimetric analysis (TGA) patterns of Feldspar–KH_2PO_4 samples that were milled for 2 h at different milling speeds were shown in Fig. 3.

Figure 3 shows that feldspar did not present significant mass loss during TGA analysis, with a mass loss of 0.5%.

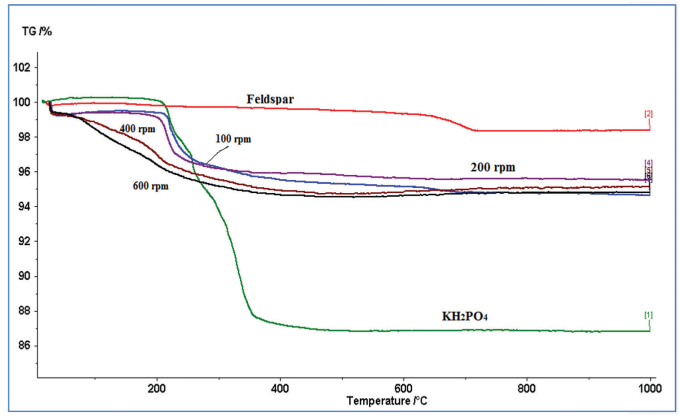

Figure 3. The TGA patterns of Feldspar–KH_2PO_4 sample mixtures were milled for 2 h at various mill speeds.

This small loss shall be related to the evaporation of impurities like carbonates and the free water elimination of feldspar, which is a good match for the predicted value of 0.3% (10), demonstrating the high purity of the feldspar that was employed. The phosphate salts generally disintegrate in three steps, starting endothermic peaks at 230°C, 270°C, and 360°C for potassium dihydrogen phosphate (Fig. 3). For samples milled at 100 and 200 rpm, clear mass loss obtained at 230°C illustrated that these low speeds of rotation were not enough to incorporate KH_2PO_4 into feldspar, Nevertheless, no mass loss characteristics of the raw materials were observed in the milled samples of potassium dihydrogen phosphate milled at 400 and 600 rpm, which indicates that they are destroyed during grinding; this is in agreement with the observations of other instrumental techniques showing that amorphous phases were formed by combining the reagents.

Figure 4 depicts the 24-h release curve of K^+ and PO_4^{3-} nutrients from Feldspar–KH_2PO_4 sample mixes milled at varied rotating rates can be determined. As shown by the results from samples prepared at 100 and 200 rpm, the release of both K^+ and PO_4^{3-} reached around 1,003 and 983 ppm, respectively. These results indicate a greater mill rotational speed is required for complete amorphization of the starting materials to incorporate KH_2PO_4 into the amorphous feldspar structure. As the mill speed was increased from 400 to 600 rpm, the release of kaolin and phosphate nutrients into the solution decreased markedly. This was achieved by reaching 974 ppm at 400 rpm and sharply decreasing to 484 ppm at the sample. This suggests 600 rpm, suggesting the addition of KH_2PO_4 to feldspar in amorphous form. Specifically, metals such as Al and Si, especially those that are present in Al-Si-O networks, retard the diffusion movement of these elements (Lee et al., 2003). In water, both K^+ and PO_4^{3-} dissolve as a result of KH_2PO_4, and these chains are attached to Al–Si–O molecules.

A correlative study with Kaolinite–KH_2PO_4 [3] is investigated to make sense and clarify the effect of milling speed

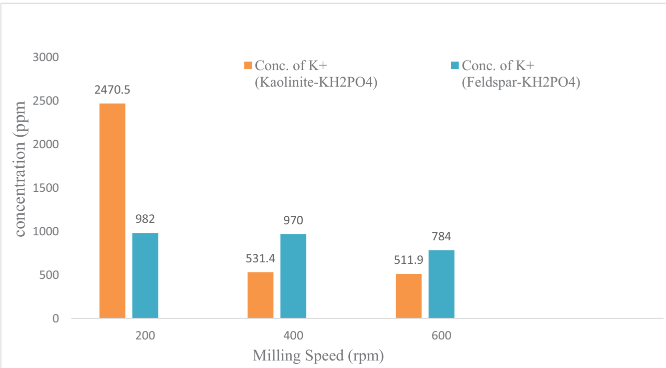

Figure 4. The profile of nutrient release of feldspar–KH_2PO_4 samples, determined after milling at a variety of mill speeds for 2 h and dispersing them in water for 24 h.

Table 2. Collected results of K^+ nutrients in (ppm) released from KH_2PO_4 incorporated with kaolinite/feldspar, milling for 120 min at a different milling speed.

Milling Speed (rpm)	Conc. of K^+ (Kaolinite–KH_2PO_4) [3]	Conc. of K^+ (Feldspar–KH_2PO_4)
200	2470.5	982.0
400	531.4	970.0
600	511.9	784.0

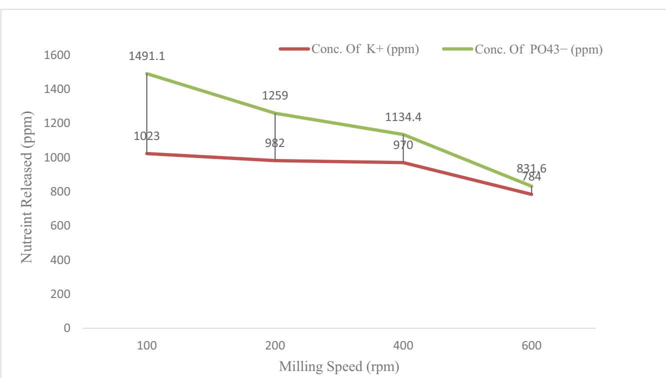

Figure 5. Correlation process between conc. K^+ released from Kaolinite–KH_2PO_4 and Feldspar–KH_2PO_4 complexes with different milling speed.

at a fixed wt ratio and milling time to the release of K^+ from different complexes when dispersed into distilled water for 24 h; the results are displayed together in Table 2.

Figure 5 clarifies the correlation process between Kaolinite–KH_2PO_4 [3] and Feldspar–KH_2PO_4 complexes results in Table 2, examining the effectiveness of these complexes as SRF by milling at 600 rpm for various time intervals and comparing the nitrogen release results to determine which one is the most suitable as SRF.

Table 2 and Figure 5 demonstrate that it is possible to reduce disintegration of K+ nutrients by increasing milling speed, which is in agreement with IR, TGA, and XRD results [3]; however, results refer that Kaolinite-$KH_2PO_4$is more suitable than feldspar as a nutrient carrier and best for use and application as SRF.

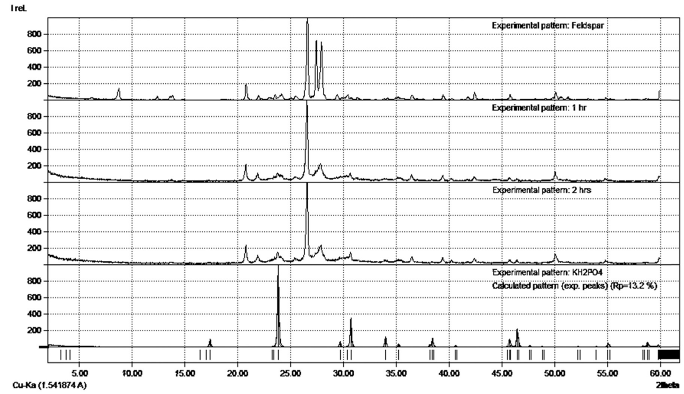

Figure 6. The XRD patterns of Feldspar–KH_2PO_4 samples were milled for different periods at a speed of 600 rpm.

Feldspar–KH_2PO_4 as SRF: Effect of milling time

Amorphization of the Feldspar–KH_2PO_4 sample mixture was studied using the XRD patterns shown in Figure 6. Throughout all experimental runs, milling speed was fixed at 600 rpm, and milling intervals ranged from 60- to 180-min. As can be seen in Figure 6, most of the characteristics associated with KH_2PO_4 had been removed from milled products at a lower milling time of about 60 min. Furthermore, using a 120-min milling time, KH_2PO_4 was reduced to an amorphous state and the featured peaks disappeared, supporting the idea that KH_2PO_4 was incorporated into the amorphous structures of the feldspar.

As can be seen in Figure 7, the thermal dehydroxylation of the feldspar caused a mass loss of 0.3%. In the milled samples, potassium dihydrogen phosphate, the mass loss characteristics were not observed, which could indicate their destruction in the process of grinding. This was confirmed by other instrumental methods that showed that amorphous phases originated from the reagent mixture. Additionally, Figure 7 shows that 3 h of milling resulted in just one mass loss event; however, samples milled for 60 and 120 min showed two additional mass losses, suggesting that milling duration affects mechanochemical synthesis.

Figure 8 illustrates how nutrients are released from samples milled to 600 rpm as a function of milling time after 24 h of leaching in distilled water. Both K^+ and PO_4^{3-} were detected at over 927 ppm in sample mixtures that were prepared after 60 min of milling time. This indicates sufficient milling time was required to cause complete amorphization of the starting materials to allow KH_2PO_4 to be incorporated into the amorphous feldspar structure.

During milling for 180 min, both K^+ and PO_4^{3-} nutrients were released substantially less, reaching around 708 and 653.8 ppm and reaching more than 780 ppm for samples obtained from milling at 120 min. This indicates that KH_2PO_4 had sufficient time at 120 min to incorporate into the structure of feldspar. Milling for long periods may cause the compound to escape slightly from feldspar.

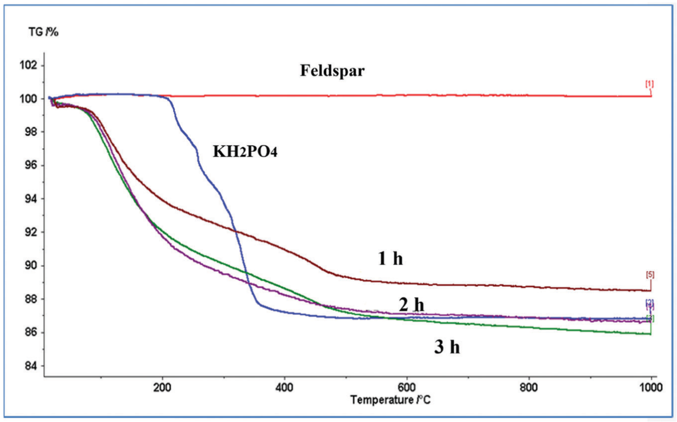

Figure 7. Patterns of TGA measurements on Feldspar–KH_2PO_4 samples milled at 600 rpm for different periods.

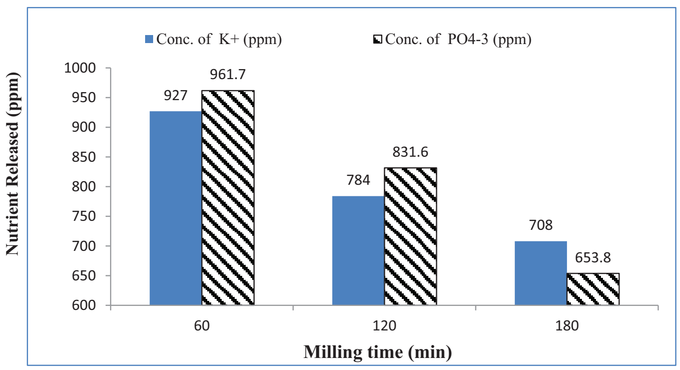

Figure 8. A nutrient release profile for Feldspar–KH_2PO_4 sample mixtures milled at 600 rpm at different milling times and dispersed in water at different times.

CONCLUSION

A novel Feldspar–KH_2PO_4 mixture loaded with KH_2PO_4 demonstrated remarkable mobility in solution because of the nutrient release characteristics of KH_2PO_4, which confirmed that, in addition to being simple and economical, the mechanochemical route also proved to be effective for synthesizing Feldspar–KH_2PO_4 complex samples that act as intelligent fertilizers. By optimizing the ratio of feldspar to fertilizer (3:1 wt ratio) and milling speed at 600 rpm for 2 hours, this study illustrated the ability to open a novel approach to the preparation of SRF and higher possibilities for the preparation of low-cost precursor biomass material. The nutrient results indicated that KH_2PO_4 had a sufficient time and milling speed to incorporate KH_2PO_4 into the structure of feldspar.

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