



Research paper

Mechanochemical activation of phlogopite to directly produce slow-release potassium fertilizer

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ABSTRACT

Phlogopite, one trioctahedral mica, was activated by solvent-free ball milling to serve directly as slow-release potassium fertilizer. Before the final breakdown of the crystal structure, phase transformation of trigonal phlogopite into monoclinic by milling at 300 rpm for 120 min was observed for the first time. Different solubility of the amorphous product and monoclinic crystalline product in water or 2% citric acid was also obtained. The content of water soluble potassium (quick acting potassium) and 2.0% citric acid soluble one (slow release potassium) in the products could be easily changed by adjusting the milling speed depending on the requirement for plant growth. 100.0% K extraction in 2.0% citric acid solution from the amorphous sample and near 30% K extraction in water from the sample milled at 300 rpm was achieved. Several analytical methods such as XRD, SEM, FT-IR and TG-DTG were used to characterize the activated sample and to understand the reason for the easier dissolution of potassium. The proposed process was economical and environment-friendly, which could help to maintain a balanced supply of potassium fertilizer for sustainable development of agriculture by compensating partially current high-cost chemical fertilizer.

1. Introduction

Potassium is a primary nutrient for the growth of plants and plays a key role for modern agriculture (Borges et al., 2017). Potassium is mainly recovered from several evaporative minerals such as sylvite and carnallite, which are abundant on earth but with extremely unbalanced distribution. Potassium deficiency in the soil exists in many areas of the world and directly affects the sustainable development of local agriculture. On the other hand, potassium exists in many water insoluble minerals such as mica, alunite and K-feldspar and no feasible technology is currently available to utilize these solid minerals. Among mica, muscovite and phlogopite may contain about 10% potassium and are widely available around the world. Mica is widely used in several fields, and massive waste mica is left when well crystalline sample is used (Miskovsky, 2004). Utilizing these unexploited potassium sources allows a balanced supply of potassium fertilizer and may play a key role in raising the security for stable development of agriculture.

Nutrient loss of fertilizer from flood or permeation happens commonly when using current highly soluble chemical fertilizers especially in the rainy area, which surely increases agriculture production cost

and results in water eutrophication (Borges et al., 2017; Camargo and Alonso, 2006). The concept of using slow-release fertilizer (SRF, also known controlled release fertilizer) is widely accepted to overcome these problems (Guertal, 2009). Many techniques including polymer coating over fertilizer particles have been developed to produce commercial SRF. Based on the background, a new approach is proposed to transform the unexploited minerals directly into SRF products, simply by mechanochemical activation.

The solvent-free mechanochemical processes offer a green option for the material and chemical industry (Qu et al., 2016a; Qu et al., 2016b; Wang et al., 2016). Mechanochemical method has been applied to replace the polymer coating in the production of SRF (Li et al., 2017; Alshamaileh et al., 2017; Borges et al., 2015). Co-milling of clay minerals such as talc (Borges et al., 2017), kaolinite (Solihin et al., 2011) with chemical K, N, P salts could produce high-quality SRF. Our previous work (Zhang et al., 2009; Solihin et al., 2010; Yuan et al., 2014) reported mechanochemically induced solid state reactions to prepare SRF by ball-milling kaolinite or Al₂O₃ with soluble K, N or P salts. However, in these cases, chemical salts of potassium/ammonium phosphates have to be used as starting sample, which still relies on the current fertilizer production. Direct transformation of natural minerals

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into SRF possesses obvious advantages of low cost and environmental-friendliness.

Excessive comminution of mica was a common phenomenon in the mica processing industry to produce massive waste mica. To recycle the waste mica and remedy the deficiency of K in the soils, the exploitation of waste mica seems to be an alternative option. Phlogopite, a typical mica, contains 7%–10% K_2O . Several methods of K extraction have been proposed such as the saturated nitrate barium solution (Meng et al., 2016), extraction of potassium in mica by sulfuric acid (Luo et al., 2015), the decomposition of phlogopite by hydrochloric acid (Kuroda, 1978). The reported methods for the extraction of potassium from phlogopite normally involved the use of acidic solutions to produce numerous waste water. A clean process is needed for the recovery of K for phlogopite.

The amorphization of clay minerals containing hydroxyl group after the milling operation has been confirmed in many previous publications (Hongo et al., 2012; Huang et al., 2017; Petra et al., 2017), which may suggest possible solubility in acid environment. In this study, phlogopite was chosen as starting sample and subjected to high energy ball milling to examine the possibility of directly transforming it into SRF. The relationship between the solubility in citric acid as the indication of slow release and the changes in crystalline structure due to ball milling was studied to understand the mechanism. Extension of the proposed environment-friendly process to other natural minerals to produce high-quality SRF and partially replace the current chemical fertilizer is highly expected to contribute to the sustainable development of agriculture.

2. Materials and methods

2.1. Materials and methods

A phlogopite sample from Bazhou, Xinjiang, China was used in this experiment. The sample was first ground into powder ($< 150 \mu\text{m}$) by a prototype milling (RK / X. ZM-100, Wuhan Rock, China). 2.0 g of phlogopite powder was then put in planetary ball milling (Pulverisette-7, Fritsch, Germany) which was equipped with two pots of zirconia (45 cm^3 of internal volume) with 7 zirconia balls of 15 mm in diameter. The rotational speed was varied from 0 to 600 rpm while the milling time was fixed at 120 min. X-ray diffraction characterization of the prepared samples was carried out using MAX-RBRU-200B, Rigaku, Japan. Fourier transformed infrared (FT-IR,) spectra of the samples were scanned over $4000\text{--}450 \text{ cm}^{-1}$ on Nicolet 6700 Thermo USA, using KBr as a diluent. Scanning electron microscopy (SEM) (JSM-5610LVJEOL, Jeol, Japan) was used to observe morphology change.

2% Citric acid solution (Sinopharm Group Co Ltd., Shanghai, Analytical reagent) was used to evaluate the slow-release features. In each experiment, 0.05 g of the milled sample was dispersed in 100 ml of distilled water and citric acid, respectively, stirred on a magnetic stirring apparatus (524G, Meiyongpu Shanghai, China) for 120 min at 500 rpm under room temperature. After that pH of the solutions was measured using a pH Meter (Seven compact, Mettler Toledo, Switzerland). The suspension was centrifuged to remove the solid to measure the concentration of potassium in each supernatant using Atomic Absorption Spectrometry (AA 6880, Shimadzu, Japan) for the calculation of K extraction rate. Element analysis of raw phlogopite was carried out by X-ray fluorescence spectrometer (XRF) on Axios advanced, Netherlands, Malvern Panalytical.

3. Results and discussion

Fig. 1 displays the phase transformation of phlogopite with milling speed varied at 0 rpm, 300 rpm, and 600 rpm. The phlogopite without milling was a pure phase without other observable impurities. K content of 8.3% by chemical analysis was near to the theoretical 9.3% with the formula $\text{KMg}_3[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ for phlogopite, indicating the high

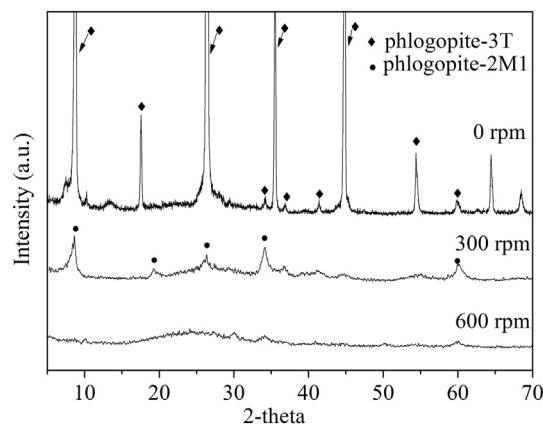


Fig. 1. XRD patterns of phlogopite milled at different speeds.

Table 1

Chemical compositions of the phlogopite sample.

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO
0.24	0.45	6.33	61.77	0.07	1.70	10.60	8.53	0.24	0.04
Fe ₂ O ₃	CuO	ZnO	As ₂ O ₃	Rb ₂ O	SrO	ZrO ₂	BaO	PbO	F
2.08	0.05	0.24	0.01	0.01	0.08	0.02	1.76	0.14	2.97
Cl	loss on ignition								
0.04	2.64								

purity. Chemical compositions of phlogopite were listed in Table 1. When the milling operation of 300 rpm was introduced to activate the sample, the intensity and full width at half maximum (FWHM) of the reflections were significantly lower and wider than that of the raw phlogopite, indicating a partial breakdown of the phlogopite crystal structure and grain refinement. XRD pattern of the 600 rpm milled sample exhibited no diffraction reflections, indicating that the structure of phlogopite was completely damaged to transform into a glass-like amorphous state by the high energy ball milling. The three strong reflections of the phlogopite were 10.08 Å, 3.37 Å and 2.02 Å, corresponding to the d_{003} , d_{009} and d_{0015} of phlogopite-3T (JCPDS 10-0492) (Schingaro et al., 2013) which crystallized in the trigonal system. The three strong reflections of the 300 rpm sample were 10.25 Å, 2.62 Å and 3.37 Å which could be assigned to the d_{002} , d_{006} and d_{116} of phlogopite-2M1 (JCPDS 10-0493) (Scordari et al., 2012) of a monoclinic system. It is very interesting to note that, before the complete breakdown of the crystal structure, phase transformation of phlogopite from trigonal to monoclinic happened at relatively mild milling condition at 300 rpm and was reported here for the first time. This is different from the commonly observed phenomena with other clay minerals such as kaolinite, serpentine, talc or pyrophyllite, of which gradual amorphization is usually observed without appearances of other intermediate phases. (Huang et al., 2017; Solihin et al., 2011).

The release rates of potassium from the milled phlogopite in distilled water and 2% citric acid with different rotation speed are shown in Fig. 2. In distilled water, the extraction of K from the natural powder (0 rpm) was 2.37% which could be attributed to the dynamic equilibrium of K^+ concentration in the water solution. There was an increase in potassium extraction with milling speed up to 300 rpm and then a gradual decline with further increase in milling speed during 400 rpm–600 rpm. The highest extraction rate of K^+ from phlogopite was 27.38% in distilled water (rotation speed 300 rpm), indicating that most of the K in the phlogopite was still retained in the structure which was crucial to serve as SRF. A 2% citric acid solution, well accepted concept to give similar environment around the roots of plants to ensure the possible adsorption of the nutrients, was applied to K extraction. The K extraction rate was continuously increased with the increase

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