Sustainable and clean utilization of coal gangue: activation and preparation of silicon fertilizer

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Abstract
Coal gangue, a by-product produced during the coal processing, has a serious impact on the environment. Using coal gangue as a fertilizer has been proven helpful in potentially reducing its environmental impact and improving its value. In this study, the formation mechanism and influencing factors of coal-gangue-based silicon fertilizer was studied using XRD and FT-IR measurement technologies. The results showed that the layered structure of coal gangue was severely damaged above 600 ℃, where the kaolin began to transform into metakaolin. When CaCO3 alone was added, CaCO3 mainly played a catalytic role, forming only a small amount of calcium silicate with available-Si content below 12.60%. When corn stalk powder alone was added, the oxides of the corn stalk ash participated in the chemical reaction involving coal gangue, forming nepheline (K(Na, K)3Al4Si4O16) and other silicates with available-Si content of 14.56%. When coal gangue, CaCO3, and corn stalk powder were mixed and calcined, the available-Si content was as high as 22.97% under the synergistic effect of CaCO3 and corn stalk powder; the concentration of toxic metals and ions was below 52.87 mg/kg. The prepared silicon fertilizer can reduce the pollution of coal gangue and meet the agricultural needs of China.

Keywords Coal gangue · Available-silicon · Diffraction peak · High-temperature calcination · Silicon fertilizer

Introduction
As the second most abundant element in the soil, silicon (Si) is ubiquitous in plants, and plays a vital role in the growth of some crops [1–3]. However, only monosilicic acid below 1% in the soil can be absorbed and utilized by plants, and is called available-Si. Moreover, with the continuous promotion of the large-scale agricultural model in China, the available-Si in the soil gradually decreases, which may have a potential negative impact on plant growth [4, 5]. Therefore, scientific and reasonable application of silicon fertilizer for the timely supplementation of the available-Si in the soil has become a focus of modern agricultural production [6, 7]. Silicon fertilizer comes mainly from two sources. The first source is the water-soluble silicon fertilizer formed through the artificial combination of water glass (or quartz sand) and carbonates, with the available-Si above 60%. However, the production cost of water-soluble silicon fertilizer is relatively high with lower yield, making it difficult to meet the large demand for silicon fertilizer in modern agriculture from this source [8–10]. On the other hand, steel slag from industrial solid waste, slag, fly ash and black liquor from the paper industry can be activated to form the citrate-soluble silicon fertilizer, which has a low effective silicon content, mostly less than 35%. The silicon fertilizer so produced has a delayed effect but exhibits high performance, and is effective over a long period; it also realizes the secondary resource utilization of solid waste while mitigating environmental pollution, which has high developmental and application prospects [11].
Coal gangue, which is the main source of citrate-soluble silicon fertilizer, is a solid waste produced in the process of coal processing and utilization. Due to the accumulation of a large amount of coal gangue and the failure to fully utilize or dispose of it, it caused problems on the environment in the air pollution and water pollution, and triggered some geological disasters such as landslides and coal gangue debris flows [12]. Fortunately, coal gangue is a type of low-carbon, hard black rock with SiO₂ as its main component, accompanied by abundant trace elements such as B, Cu, Co, Zn, and Mn. The Si component of coal gangue is suitable for producing silicon fertilizer, while the presence of trace elements can promote crop growth and development [13], which can improve resource utilization and reduce the pollution of coal gangue. However, since the silicon in coal gangue cannot be directly absorbed and utilized by plants, it is necessary to convert crystalline silicon dioxide into available-Si that can be absorbed and utilized by plants, so as to realize its use in agriculture. The activation processes commonly used at present to achieve this end are mainly divided into four types, namely mechanical activation, microbial activation, chemical activation and high-temperature activation.

In the mechanical activation process, mechanical energy is mainly used to cause physical and chemical changes in the target mineral, which promotes imperfections or displacements in the crystal lattice and even the amorphous state, thereby improving the dissolution behavior of useful chemical components [14]. Liu et al. [15] used mechanical grinding to activate potassium-containing silicate minerals, thereby increasing the release of silicon and potassium, to prepare silicon–potassium fertilizers. Countries such as Japan and North Korea often adopt this activation method for the preparation of silicon fertilizer, achieving good economic benefits in rice cultivation [16–18]. However, the available-Si content of the silicon fertilizer produced by mechanical activation is generally low, which is insufficient to meet the needs of large-scale agricultural production. The aim of the microbial activation process is mainly to degrade the target minerals using the metabolic process of the microorganisms themselves (i.e., use of silicate bacteria and bacillus megaterium) to achieve the dissolution of P, K and Si, thereby producing microbial fertilizers [19]. The microbial activation process exhibits high efficiency in dissolving P and K from coal gangue, but its efficiency in dissolving Si is relatively low [20–22]. The chemical activation process mainly uses acid, alkali, and salt solutions to destroy the chemical bonds in the target minerals, thereby increasing the available-Si [23]. However, this process is currently in the laboratory stage of development. Sun et al. [24] activated a mixture of coal gangue and straw in KOH and H₂O₂ solutions to prepare silicon fertilizer, but the Si that was finally available in the activated coal gangue was only approximately 1.0–3.5%; it is thus difficult to prepare high-efficiency silicon fertilizer using chemical activation.

The high-temperature activation process mainly utilizes a high-temperature environment to promote the reaction of target minerals with other reagents, so as to transform their stable structure into a morphological structure with multiple micropores, multiple broken bonds, increased solubility, and higher internal energy. Finally, the Si in the target mineral is activated into available-Si [25, 26]. To improve the rate of extraction of available-Si from the target mineral at high temperature, activators such as calcium carbonate, potassium carbonate, sodium carbonate, diethanolamine and alkali metal salts are necessary, the reactions resulting in citrate-soluble silicon fertilizers such as silicon–potassium fertilizer, silicon calcium fertilizer and silicate micro-fertilizer. Yao et al. [27] used steel slag as a raw material and prepared a fused potassium silicate fertilizer at high temperature by adding potassium carbonate. It has been reported that the preparation of silicon fertilizer by high-temperature activation is a very viable and relatively simple process which is particularly suitable for industrial applications. However, few studies have been carried out on the preparation of coal-gangue-based silicon fertilizer using high-temperature activation technology.

In this study, coal gangue mixed with calcium carbonate and corn stalk powder is used as a raw material to produce gangue-based silicon fertilizer through high-temperature activation. Combining X-ray diffraction (XRD) and Fourier transformed infrared (FT-IR) measurement with siliconolybdenum blue spectrophotometry, the influence of calcination temperature and mixing ratio on the available-Si in activated coal gangue was initially explored; the optimal preparation procedure was then investigated. Finally, the leaching test was used to study the release characteristics of coal-gangue-based silicon fertilizer, and its reliability verified, thereby providing a theoretical basis for use of coal-gangue-based silicon fertilizer in agriculture.

Materials and methods

Materials

Coal gangue

The coal gangue used in the experiment comes from the Shendong mining area in Inner Mongolia, China, with an ash content of ~ 85.60%. To facilitate calcination, the coal gangue was ground to ~ 200 mesh.
Corn stalk powder

The corn stalk powder (Zea mays L. Yufeng 303) comes from farmland near the Shendong mining area in Inner Mongolia, China. For better mixing of the sample, the corn stalk powder was ground to − 200 mesh size. The elemental analysis (i.e., carbon, hydrogen, nitrogen, sulfur, and oxygen) of raw corn stalks were obtained by the Thermo Scientific FLASH 2000 Elemental Analyzer (FLASH2000, Thermo Fisher Scientific, USA) shown in Table 1; and the chemical composition of corn stalk ash at different calcination temperatures were characterized using X-ray fluorescence spectrometry (XRF) (Bruker S8 Tiger, Bruker AXS, German) shown in Table 2.

Table 1 shows that raw corn stalks contain more oxygen elements, which can provide a certain chemical oxygen demand during the combustion process, thereby improving the combustion efficiency; while the carbon elements are mostly discharged in the form of carbon dioxide during the combustion process, which is not conducive to the subsequent chemical reactions process. After high-temperature calcination, a large amount of oxides appeared in corn stalk ash, and the oxide contents of corn stalk ash are roughly the same at different calcination temperatures shown in Table 2. The main oxides are SiO2, K2O, CaO and MgO, which react with the silica-containing ore in coal gangue, thereby promoting the activation of Si in the coal gangue.

Methods

In this study, coal gangue (10 g sample for each experiment) mixed with CaCO3 and corn stalk powder was used to prepare coal gangue-based silicon fertilizer using a high-temperature activation furnace (DC-B-2, Beijing Original Technology Co., Ltd., China). For the high-temperature calcination process to be completed, the mixture were transferred into the activation furnace (air atmosphere) for 120 min after the temperature of the activation furnace reached the predetermined value, where the calcination was under normal atmospheric pressure without special gas. Moreover, using XRD (D8 Advance, Bruker Axs GmbH, German) and FT-IR (Vertex 80v, Bruker Axs GmbH, German) measurement technologies, the changes in the composition of crystalline phase and functional groups of the samples were obtained to analyze the mechanism of formation of silicon fertilizer from coal gangue. Herein, the X-ray generator was equipped with a copper target X-ray tube operating at 40 kV and 26 mA (radiation wavelength λ = 0.154 nm). In the measurement process, XRD spectra were acquired at room temperature over the 2θ range of 5° – 35° at 0.05° intervals with a measurement time of 1 s per 2θ intervals. Moreover, FT-IR spectra were obtained on KBr pellets (1 mg of samples powder and 200 mg of KBr, pressed into 13 mm diameter discs at a pressure of 10 Ton). FT-IR spectra were recorded on a Bruker Vertex 80v Fourier Transform Infrared Spectrometer with a resolution of 4 cm−1, by 64 scans in the region between 4000 and 450 cm−1. In addition, the soluble silica concentrations of the sample were extracted by 0.5 M HCl with a S/L ratio of 1:200 and horizontally shaken at 150 r/min for 8 h, and then determined through the silicon molybdenum blue spectrophotometry [7]. To analyze the influence of various factors on the activation process, the available-Si content as the evaluation standard needs to be converted by the following equation:

\[ k = k_o \times 0.4674 \]  

(1)

where \( k \) is the available-Si content of the sample, as %; \( k_o \) is the soluble silica concentrations of the sample, as %.

In addition, to improve the accuracy of the experimental results, all experiments were repeated three times, and the average of the three results was used as the final result.

| Sampling | Elemental content (%) |
|----------|-----------------------|
| Corn stalk | H | C | N | O | S | Others |
| 5.01 | 45.87 | 2.26 | 38.62 | 0.93 | 7.31 |

| Temperature/℃ | SiO2 | Al2O3 | Fe2O3 | K2O | CaO | MgO | SO3 | P2O5 | Na2O | MnO | Cl |
|---------------|------|-------|-------|-----|-----|-----|-----|------|------|-----|----|
| 200 | 60.82 | 0.99 | 1.03 | 16.31 | 9.25 | 1.67 | 1.32 | 1.14 | 0.18 | 0.36 | 4.19 |
| 400 | 61.36 | 1.04 | 1.26 | 15.10 | 10.07 | 1.71 | 1.45 | 1.68 | 0.11 | 0.20 | 3.01 |
| 600 | 62.07 | 1.25 | 1.30 | 14.21 | 10.80 | 1.51 | 1.51 | 1.81 | 0.08 | 0.12 | 2.63 |
| 800 | 66.75 | 1.31 | 1.35 | 11.02 | 11.04 | 1.02 | 1.71 | 2.01 | 0.01 | 0.02 | 1.02 |
| 1000 | 67.25 | 1.49 | 1.41 | 11.07 | 11.05 | 1.02 | 1.71 | 2.01 | 0.01 | 0.02 | 0.92 |
Single-factor exploration

To analyze the influence of the calcination temperature, the mixing ratio of CaCO₃ (or corn stalk powder) to coal gangue, and the available-Si content in the activated coal gangue produced—corresponding to five levels for each factor to be studied—were determined, and are shown in Table 3.

Multi-factor optimization

To obtain the optimal mixing ratio of coal gangue, CaCO₃ and corn stalk powder for the efficient preparation of coal-gangue-based silicon fertilizer, 25 sets of mixed calcination experiments were performed, the results of which are shown in Table 4.

Leaching experiment

The release characteristics of toxic metal ions were studied to verify the safety and applicability of the coal-gangue-based silicon fertilizer. Herein, the most commonly used batch leaching methods, i.e., the Toxicity Characteristic Leaching Procedure (TCLP), was adopted [28]. Herein, the silicon fertilizers were soaked in 0.1 M Glacial acetic acid with a S/L ratio of 1:20 and pH of 2.88, followed by cyclotron oscillation at 30 r/min and 23°C for 18 h, and then the toxic metal ions content of the leachate were determined by the inductive coupled plasma emission spectrometer (ICP) (Varian 820-MS, VARIAN, USA) to verify the reliability of silicon fertilizer.

Results and discussion

Results

Single-factor exploration

The coal gangue was subjected to calcination under various operating conditions, as shown in Fig. 1. The available-Si in coal gangue is different at different calcination temperatures, showing a gradually increasing trend with increase in temperature. When the calcination temperature reaches 600 °C, the available-Si increases rapidly; while available-Si is 6.18% at 400 °C, it is 8.19% at 600 °C, the value then increasing slowly with temperature, indicating that the Si component of coal gangue is activated at 600 °C. However, the overall percentage of available-Si is not high (k < 10%).

In the subsequent experiments where calcination is carried out after mixing CaCO₃ and then corn stalk powder, the calcination temperature is set to 600 °C. In the calcination experiment involving coal gangue mixed with CaCO₃, the available-Si content of the calcined coal gangue is significantly larger than that of the calcined coal gangue obtained through the calcination of coal gangue alone. With the increase of the mixing ratio, the available-Si content of calcined coal gangue increases slightly. Especially, when the mixing ratio of coal gangue and CaCO₃ increases to 1:0.9, the available-Si content can reach 12.60%, indicating that CaCO₃ can promote the activation process of coal gangue to a certain extent.

When coal gangue and corn stalk powder are mixed and calcined, available-Si increases with increase in mixing ratio. When the mixing ratio is 1:0.9, the available-Si content rises to 14.56%, which is obviously larger on the whole than that in activated coal gangue mixed with CaCO₃; this may be due to the influence of oxides formed by the calcination of corn stalk powder.

Table 3  The levels of each factor

| Factors                                      | Value       |
|----------------------------------------------|-------------|
| Calcination temperature                     | 200°C 400°C 600°C 800°C 1000°C |
| Mixing ratio of CaCO₃ (i.e., gangue:CaCO₃)   | 1:0.1 1:0.3 1:0.5 1:0.7 1:0.9 |
| Mixing ratio of corn stalk powder (i.e.,    | 1:0.1 1:0.3 1:0.5 1:0.7 1:0.9 |
Fig. 1 Available-Si content of calcined coal gangue under different conditions

Fig. 2 Available-Si content of samples under different conditions
Multi-factor optimization

To study the trends in available-Si during the calcination of coal gangue mixed with CaCO₃ and corn stalk powder, a multi-factor experiment was used to obtain the best mixing ratio in each case, as shown in Fig. 2.

Overall, during the mixed calcination process, available-Si increases with the increase of CaCO₃ (or corn stalk powder); there were two peaks, with available-Si of 22.97% and 22.55% at mixing ratios of 1:0.3:0.9 and 1:0.9:0.9, respectively. Moreover, the available-Si content of the activated samples basically meets the relevant regulations on silicon fertilizer (NY/T797-2004, China), i.e., \( k > 10\% \), which indicates that it is feasible to use a mix of coal gangue, CaCO₃ and corn stalk powder to form a silicon fertilizer through calcination. From an economic point of view, to produce efficient coal-gangue-based silicon fertilizer, the optimal mixing ratio of coal gangue, CaCO₃ and corn stalk powder should be 1:0.3:0.9.

Leaching experiment

According to TCLP, the main toxic metal ions, i.e., Cr, Pb and Ni, in the leachate from coal-gangue-based silicon fertilizer have the highest value of 52.87 mg/kg, 32.98 mg/kg and 32.20 mg/kg, respectively (Table 5). Therefore, the concentrations of toxic metal ions in coal-gangue-based silicon fertilizer meet the safety requirements for agricultural applications according to the relevant standards for fertilizers, where the concentrations of toxic metal ions are lower than the Chinese Agricultural Fertilizer Control Standard (250 mg/kg Cr, 200 mg/kg Ni, 250 mg/kg Pb, 75 mg/kg As, 5 mg/kg Cd) (GB 8173–1987 and GBT 29,163–2012).

Discussion

Calcination temperature

Figure 3 is the FT-IR spectrum of coal gangue, with its characteristic absorption curve. Here, 3697 cm⁻¹ and 3620 cm⁻¹ are the vibrations in the outer hydroxyl group (i.e., structural water) and inner hydroxyl group (i.e., interlayer water), respectively, of kaolin in raw coal gangue [29]; the absorption peak at 1430 cm⁻¹ is mainly formed by hydroxyl bending vibration. The adsorption peaks at 942 cm⁻¹ (back peak) and 912 cm⁻¹ correspond to the bending vibrations of the inner surface hydroxyl group and inner hydroxyl group, respectively [30, 31], and the absorption peaks at 1100, 695 and 473 cm⁻¹ are attributed to the stretching vibration.
flexural vibration and rocking vibration of the TOT bond where T is Al and Si [32]. Moreover, the absorption peaks at 539 and 431 cm\(^{-1}\) may be attributed to Si–O–Al\(^{VI}\), which overlaps with the absorption vibration of the Si–O–Si bond [33].

When the calcination temperature reaches 600 °C, the characteristic peaks of the hydroxyl groups are replaced by a series of new absorption bands, indicating that the layered structure of coal gangue has been completely damaged. With the disappearance of the absorption peaks at 1100, 1033 and 1009 cm\(^{-1}\), a strong and broad absorption peak appeared at 1050 cm\(^{-1}\), which corresponds to the stretching vibration of the TOT bond in metakaolin, indicating the presence of metakaolinite in the calcined sample. The characteristic absorption bands of metakaolinite also contained the three newly formed bands corresponding to Si–O–Si bond vibration at 798 cm\(^{-1}\) and Si–O bending vibration at 694 and 486 cm\(^{-1}\) [34]. Moreover, the original absorption peaks at 539 and 432 cm\(^{-1}\) disappeared, indicating the transition from Si–O–Al\(^{VI}\) to Si–O–Al\(^{IV}\), which is also evidence of the formation of the amorphous metakaolinite phase. Therefore, calcination temperatures above 600 °C can promote the phase change of coal gangue, rapidly increasing its available-Si content.

The diffraction peaks in the XRD spectra of coal gangue samples are different at different temperatures shown in Fig. 4. From the XRD spectrum, the raw coal gangue is seen to be mainly composed of quartz, kaolinite and muscovite. Si in coal gangue exists mainly in the form of SiO\(_2\) and silicate, which have relatively stable phase structures, requiring activation treatment to produce effective silicon fertilizer.

When the temperatures are lower than 600 °C, the diffraction peaks of coal gangue samples show little change, indicating that the composition and structure of coal gangue before and after heat treatment are similar, mainly composed of quartz, kaolinite and muscovite. The intensity of individual diffraction peaks corresponding to quartz increases with the increasing temperature, which may be caused by the burning of residual carbon in coal gangue, and the formation of amorphous SiO\(_2\) during the dehydroxylation of minerals such as kaolin and muscovite. As suggested by the disappearance of individual diffraction peaks of kaolinite and the formation of calcium silicate hydrate peaks, the hydroxyl group of kaolinite is being transformed into metakaolinite. When the calcination temperature exceeds 600 °C, the diffraction peak corresponding to kaolinite gradually disappears, indicating that the kaolinite is being transformed into metakaolin at high temperature, thereby activating coal gangue. When the calcination temperature exceeds 800 °C, the diffraction peak corresponding to muscovite gradually disappears, indicating that the muscovite in the coal gangue has undergone structural changes. However, due to the relatively low content of muscovite, the increase in available-Si in the coal gangue during this phase is not significant. Therefore, when the calcination temperature exceeds 600 °C, although available-Si in calcined samples increases, the rate of increase is not significantly high.

Fig. 4 XRD spectra of calcined samples at different temperatures
Calcination of coal gangue and CaCO₃ mixture

When coal gangue is calcined with CaCO₃ at 600 °C, the characteristic absorption curve changes significantly, as shown in Fig. 5. The absorption peaks at 2874, 2513, 1799, 1421, 875 and 712 cm⁻¹ are characteristic peaks of carbonate, 3674 cm⁻¹ corresponds to the stretching vibration of the free hydroxyl group, 1048 cm⁻¹ indicates Si–O stretching vibration, and 562 and 484 cm⁻¹ correspond to the bending vibration of Si–O. Here, 3674, 1048, 562 and 484 cm⁻¹ constitute the characteristic peaks of hydroxy silicate [35], indicating that a large amount of soluble silica minerals are formed by the calcination of coal gangue mixed with CaCO₃. Moreover, increasing the mixing ratio of coal gangue to CaCO₃ does not significantly change the solid phase structure formed, but only increases the intensity of the relevant characteristic peaks, indicating that the effective extraction rate of available-Si from coal gangue increases with increase in the mixing ratio.

From the XRD spectrum of coal gangue calcined with CaCO₃ shown in Fig. 6, it is seen that the untreated coal gangue contains quartz, kaolinite and muscovite. After calcination of the mixture at 600 °C, the peaks related to kaolinite disappeared, while the intensity of the peaks related to quartz and muscovite decreased significantly with increase in CaCO₃ content. When the mixing ratio exceeds 1:0.5, there is no new crystal phase in the calcination except the formation of soluble calcium silicate, indicating that the whole activation process at this stage is a non-equilibrium reaction limited to the destruction of the crystalline structure. Moreover, this destroyed crystal structure will not evolve into crystals again, but will remain amorphous; for example, kaolinite is transformed into amorphous metakaolinite under the influence of CaCO₃. Thus, CaCO₃ mainly plays a catalytic role in the entire calcination and activation process; the only chemical reaction involving CaCO₃ is its reaction with coal gangue on the contact surface, forming soluble calcium silicate.

Calcination of coal gangue and corn stalk powder mixture

The FT-IR spectrum of the coal gangue calcined with corn stalk powder, subjected to calcination at 600 °C, mainly displays the vibration absorption peak of the metakaolinite phase (Fig. 7). Compared with the spectrum after calcination of coal gangue alone, the main characteristic peaks of the calcined mixture spectrum—such as the stretching vibration peak of the T–O–T bond at 1050 cm⁻¹—are significantly wider. Moreover, the vibration peak of the H–O–H bond appears at 1638 cm⁻¹, indicating that the organic matter in the corn stalk is continuously removed during calcination. Further, the oxides of corn stalk ash formed during calcination react with the silicon-containing material in the coal gangue to form a soluble silicate, which promotes the increase of available-Si in the coal gangue.

Figure 8 shows the XRD spectrum of coal gangue calcined with corn stalk powder, calcined at 600 °C. After calcination, the diffraction peaks related to kaolinite gradually disappear, indicating that the crystal structure of kaolinite has been destroyed; the kaolinite begins to
transform into metakaolinite. Moreover, a new mineral component appears in the calcined sample, namely nepheline (K(Na,K)$_3$Al$_4$Si$_4$O$_{16}$), which indicates that part of the metakaolinite is transformed into silicate. The calcined corn stalk powder contains various oxides such as CaO and K$_2$O, which promote the above transformation process. Thus, the oxides in the calcined corn stalk powder can participate in the chemical reactions involved in the further calcination of coal gangue; therefore, the available-Si content of coal gangue calcined with corn stalk powder...
is significantly higher than that of coal gangue calcined with CaCO$_3$.

**Calcination of coal gangue, CaCO$_3$ and corn stalk powder mixture**

In the multi-factor experiment, the coal gangue-based silicon fertilizer was produced under operating conditions that produced the best results (1:0.3:0.9). According to the ratio of the coal gangue, CaCO$_3$ and corn stalk powder under the best conditions, the effect of corn stalk powder is significantly better than that of CaCO$_3$ in the silicon activation process of coal gangue, which is verified in the previous chapter. Herein, the mixing ratio of CaCO$_3$ is small (i.e., 1:0.3) to achieve better results; this is partly explained by the fact that a small amount of CaCO$_3$ can play a catalytic role, while a large amount of CaCO$_3$ may lead to a chemical reaction with corn stalk powder, which is not conducive to the activation of silicon element in coal gangue. Further, the activation mechanism of coal gangue is analyzed as shown in Fig. 9. After calcination of the coal gangue, CaCO$_3$ and corn stalk powder mixture at 600 °C, the calcined sample contains not only the original quartz and CaCO$_3$, but also new substances with a large amount of soluble silicon components, i.e., nacrinite (NaAlSiO$_4$), potash nepheline (KAlSiO$_4$), and gray wollastonite (Ca$_5$(SiO$_4$)$_2$CO$_3$), resulting in the higher available-Si content of the calcined coal gangue. Here, the action of high temperature in the presence of CaCO$_3$ promotes the destruction of the crystal structure of kaolinite comprising the gangue, forming a large amount of metakaolinite. The metakaolinite further reacts chemically with the oxides in the corn stalk ash to form soluble silicon acid salt. Thus, under the synergistic effect of CaCO$_3$ and corn stalk powder, the silicon element in coal gangue can be effectively activated.

**Conclusion**

This study used CaCO$_3$ and corn stalks as additives to transform coal gangue into coal gangue-based silicon fertilizer through high-temperature activation. The available-Si in calcined coal gangue increases with increasing calcination temperature and addition ratio of CaCO$_3$ (or corn stalk powder). Herein, the kaolinite of the coal gangue begins to transform into metakaolinite in the calcining process of coal gangue alone at 600 °C, with the available-Si content of < 10%. When the mixture of coal gangue and CaCO$_3$ is calcined, CaCO$_3$ mainly plays a catalytic role in the entire activation process, only participating in a chemical reaction with coal gangue on the contact surface to form soluble calcium silicate; still, the effective silicon content in the calcined sample is not high, only reaching 12.60%. However, the available-Si content of calcined coal gangue increases significantly, reaching 14.56% when coal gangue and corn stalk powder are mixed with 1:0.9 and calcined at 600 °C, where a new mineral component appears in the calcined sample, i.e., nepheline (K(Na,K)$_3$Al$_5$Si$_4$O$_{16}$). Further,
when coal gangue is calcined with CaCO₃ and corn stalk powder, a large amount of soluble silicon components are formed under the synergistic effect of CaCO₃ and corn stalk powder. When the mixing ratio is 1:0.3:0.9 (coal gangue:CaCO₃:corn stalk powder), the available-Si content in calcined coal gangue reaches 22.97%, the amount of toxic metals and ions present being less than 52.87 mg/kg, thus providing an efficient and safe coal-gangue-based silicon fertilizer.

Considering how the coal gangue-based silicon fertilizer could contribute to a modern, and sustainable agriculture system, further studies including planting experiments using silicon fertilizer are necessary, to elucidate the state, variations and relationships between physical, chemical and mineralogical parameters of soils in relation to the silicon fertilizer and its role in plant growth.

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**Author contributions** All the authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by BD, CF and ZZ. The first draft of the manuscript was written by BL. The review and editing of the manuscript were written by XD and BZ, and all the authors commented on previous versions of the manuscript.

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