



## Research article

# Spectroscopic characterizations of silicate fertilizers prepared by chemical deashing of coals

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## ABSTRACT

Quality silicate fertilizers should be in great demand, and yet the production has been limited due to strict regulations on heavy metals, despite many raw materials and activation methods being used. In the chemical deashing of coals for the production of ultraclean coals, the silica gels of high purity were precipitated with little heavy metals from the acid deashing solutions, which could be used to produce quality silicate fertilizers by pulping with CaO or MgO under mild conditions. By varying the Ca/Si molar ratios, silicate fertilizers with different chemical compositions were prepared, and the active silica contents were measured and validated by ICP and colorimetric methods. For the curve of the active silica contents versus the Ca/Si molar ratios, four regions could be clearly marked with unique patterns, and quality silicate fertilizers occurred with the Ca/Si molar ratios from  $\sim 1.10$  to  $\sim 3.50$ . The pH values of the silicate fertilizers could also be divided into the same four regions with respect to the Ca/Si molar ratios, and the highest active silica content occurred at the pH value of  $\sim 11.30$  with the Ca/Si molar ratio of  $\sim 1.50$ . With the XRD investigations of the silicate fertilizers selected from the four regions, the water-insoluble  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  was identified as the contributor of active silica in the silicate fertilizers. By replacing full or part of CaO with MgO in the preparation of silicate fertilizers, the silica gels were found to preferably react with CaO, and the active silica contents grew with the increase of CaO. By referring to the model silicate fertilizers prepared in this work by varying the  $(\text{Ca} + \text{Mg})/\text{Si}$  molar ratios,  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  was also identified as the dominant in one commercial slag silicate fertilizer. Silicate fertilizers by silica gels can be helpful for secondary pollution elimination and cost reduction of coal deashing.

## 1. Introduction

Silicon has been well recognized as the beneficial plant prophylactic of broad spectrum, which can endow plants with the good tolerance to a wide range of biotic and abiotic stresses [1]. Therefore, many minerals and artificial sources have been tested for the silicon availability of plants, and the best could be the slags [2–4], which could also make nice contributions to the emission mitigations of greenhouse gases like  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , and the stabilization of heavy metals in soils [5–7]. Steel slags have been directly crushed to  $<0.178$  mm for use in the soil remediation trials [8], and the fine modifications of hot slags could be made with potassium feldspar or potassium carbonate as modifiers [3]. Generally, a variety of raw materials and activation methods have been used to prepare silicate fertilizers with available silicon of plants. For coal-derived solid wastes in particular, coal fly ashes were recently used to prepare silicon-potassium mineral fertilizers by one-step KOH hydrothermal method [9], coal slimes with or without pre-activation

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by sulfuric acid were used to prepare silica compound fertilizers by CaO–KOH mixed hydrothermal method [10], coal gangues were mixed with calcium carbonate and corn stalk powders for the preparation of silicate fertilizer at high temperatures [11], and coal gangues were also reclaimed by treating with microbial activation method for long time for the release of available silicon of plants [12].

Despite the huge demand for the silicate fertilizers of 30–50 million tons annually in China, only a fraction could be available in the market, mainly due to strict regulations on heavy metals. In recent years, alumina extractions have been realized by acid leaching of fly ashes in China, and the silica rich residues (white mud) with highly depleted heavy metals could be ideally used for the preparation of quality silicate fertilizers. Hydrothermal treatment or high temperature calcination were used for the preparation of silicate fertilizers by the white mud [13,14]. In particular, high temperature calcination should necessitate the addition of large amounts of alkalis as the fluxing agent [13], hydrothermal treatment could alleviate sodium in silicate fertilizers by using alkalis as the catalytic agent [14]. As a result, considerable sodium would have to be added or left in the silicate fertilizers prepared by the white mud, which could lead to the saline alkali deterioration of soils by long term applications [15]. In our previous work [16,17], new silicate fertilizers have been developed directly from the deashing of the alumina rich coals from the Province of Inner Mongolia of P. R. China. Deashing the coals could produce the alkali solutions and the acid solutions with the dissolved mineral elements in coals. By driving off the excessive water and acids from the acid deashing solutions of coals, the silica gels of high purity could be precipitated and separated by pressure filtering. The silica gels rich with water could accordingly react with CaO without any alkali addition, realizing finally the silicate fertilizers of near zero sodium.

Silicate fertilizers should be generally composed of mixed silicates, and the active silica content can be measured according to China Standard NY/T 797–2004 “Silicate Fertilizer”. In spite of slag silicate fertilizers being widely used, very little has been known about their physicochemical properties, such as detailed chemical compositions, pH values, and contributing phases of active silica in slag silicate fertilizers [2]. Most of work on silicate fertilizers has been focused on the beneficial effects in agronomy, such as the increased yields due to improved biotic and abiotic stresses by using silicate fertilizers [1,18]. In this work, by using the silica gels from the acid deashing solutions of coals, the silicate fertilizers were systematically prepared with varying the Ca/Si or Mg/Si molar ratios, and the physicochemical properties were investigated in details.

## 2. Materials and methods

The silica gels were precipitated and separated from the acid deashing solutions of coals, and the silicate fertilizers were prepared by the pulping the silica gels with added CaO and MgO under mild conditions. XRF, ICP and colorimetry, pH meter and XRD were used to investigate the chemical compositions, active silica contents, pH values, and phases of the silicate fertilizers.

### 2.1. Deashing of coals and preparation of silica gels

By applying an advanced deashing method which has been described previously [16,17], the alumina rich coals could be treated by alkalis and acids in sequence, producing the alkali solutions and the first acid solutions. The alkali solutions were regenerated by adding CaO, and the filter cake were treated by sulfuric acid (HA) to obtain the second acid solutions. By driving off the excessive water and acid from the combined first and second acid solutions, silica gels could be precipitated for separation by pressure filtering, as shown in Fig. 1. The silica gels were dried at 120 °C overnight to calculate the water content of ~93 %, the chemical compositions of

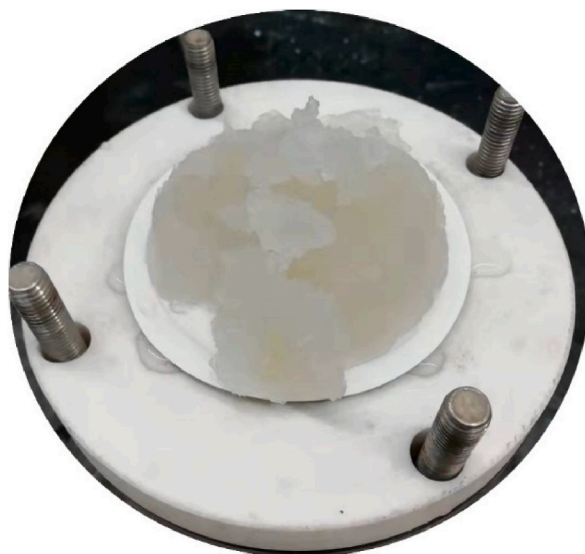


Fig. 1. Silica gels precipitated and filtered from the acid deashing solutions of coals.

dried silica gels were presented in Tables 1 and 97.71% of the total was silica ( $\text{SiO}_2$ ). By comparison with the previous results [16],  $\text{Na}_2\text{O}$  and slightly more Cl occurred in dried silica gels. In this work, silica gels were prepared in larger amounts in Fig. 1, and washings were not thoroughly made to remove all the salts formed in the deashing of coals. Nevertheless, no residual  $\text{Na}_2\text{O}$  occurred in the silicate fertilizers prepared in this work.

Depending on coals, heavy metals such as Cr, As, Cd, Pb and Hg could occur and accumulate in the chemical deashing of coals. To mitigate environmental problems, heavy metals should be detected in the coal deashing process flows [16,17], such as alkali-treated solutions, alkali-treated coals, acid-treated solutions, and acid-treated coals (i.e., ultraclean coals), and new techniques would be developed for the removal of heavy metals. Since silica gels were precipitated from acid-treated solutions, the soluble including heavy metals could be removed largely from the silica gels by filtering and multiple washings. According to China Standard GB/T 23349-2009 "Ecological index of arsenic, cadmium, lead, chromium and mercury for fertilizers", the upper limits of As, Cd, Pb, Cr and Hg were set at 50 ppm, 10 ppm, 200 ppm, 500 ppm and 5 ppm. In this work, the contents of As, Cd, Pb and Hg in dried silica gels were all below the detection limits of 8.35 ppm, 0.50 ppm, 41.51 ppm (by ICP) and 0.9 ppb (by direct mercury analyzer), and the content of Cr was 8.80 ppm (by ICP). Therefore, heavy metals should have been depleted in silica gels, providing an ideal source for silicate fertilizer preparations. At the same time, bituminous coals were deashed in this work, and very limited humic acids would enter diluted alkali solutions by forming sodium humate, which would be oxidized by alkali solutions concentrated at high temperatures.

## 2.2. Preparation of silicate fertilizers by silica gels

Unlike minerals with direct strong bonding between silica ( $\text{SiO}_2$ ) molecules or alumina ( $\text{Al}_2\text{O}_3$ ) molecules, silica gels in this work can be rich in water, which would form weak hydrogen bonds bridging silica molecules. Therefore, after filtering from the acid solutions, the silica gels were highly reactive, and CaO or MgO could be directly added for pulping reactions with stirrings at 60 °C for 0.5 h. By varying the additions of CaO and MgO, silicate fertilizers would be prepared with different chemical compositions.

## 2.3. Determinations of the active silica contents in silicate fertilizers

According to the China Standard NY/T 797-2004 "Silicate Fertilizer", the active silica content in silicate fertilizers should be measured by the weight of silica soluble in 0.5 M HCl solutions divided by the total weight. The concentrations of silicon in 0.5 M HCl solutions could be measured by ICP or colorimetry.

Due to its ability to detect total silicon, ICP has been used as the standard for silicon measurement. By comparison, colorimetric measurements were more convenient and routinely utilized in this work. According to China Standard GB/T 1574-2007 "Test method for analysis of coal", the silicomolybdate blue method builds on the fact that only monosilicic acid can react with molybdic acid for the formation of silicomolybdate yellow, which can be accordingly reduced to silicomolybdate blue for colorimetric measurements. The absorption at 630 nm was measured of silicomolybdate blue formed by monosilicic acid in diluted solutions. The standard curve has been constructed for the absorption at 630 nm versus the silicon concentration, the silicon concentrations could be directly read for the test solutions by referring to the absorption, and the active silica contents would be easily calculated. However, due to the formation of polysilicic acid in concentrated test solutions [19,20], which cannot be detected by the colorimetric method, the silicon concentrations would be underestimated. To investigate further the polysilicic acid effect, both ICP and colorimetric methods have been applied to the active silica content measurements of the same silicate fertilizers. By gradually reducing the addition of silicate fertilizers, it has been found that the solutions of silicate fertilizers could be diluted enough when ~0.1g powdered silicate fertilizers were dissolved in 0.5 M HCl solutions of 150 ml, so that the active silica contents by ICP and colorimetric methods would be very close. In this work, the active silica contents of silicate fertilizers were reported by both ICP and colorimetric methods.

## 2.4. Chemicals and instruments

The commercial slag silicate fertilizer was obtained from one manufacturer in P. R. China, and  $\text{Ca}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  of analytic grade were calcined at 850 °C for 3 h for preparation of CaO or MgO. The XRF (ZSX Primus II, Rigaku, Tokyo, Japan) was used for measurement of chemical compositions (in terms of oxides) of the silicate fertilizers after drying overnight at 120 °C. The ICP-OES (Spectro Arcos, Spectro, Kleve, Germany) was used for the silicon measurements in test solutions, and also for the detections of As, Cd, Pb, Cr in dried silica gels after digestions. The UV-Vis spectrophotometer (UV Bluestar A, LabTech, Beijing, China) was used for the colorimetric measurements of absorption at 630 nm of silicomolybdate blue formed in active silica content determinations. The direct mercury analyzer (DMA80, Milestone Srl, Milan, Italy) was used to measure the mercury in dried silica gels. The XRD (D8 Advance, Bruker, Berlin, Germany) was used for characterizations of phases in the silicate fertilizers.

The pH values of the silicate fertilizers were measured according to the China Standard NY/T 1973-2010 "Water soluble fertilizers-Determination of water insoluble matter content and pH". Measured ~1.0g powdered silicate fertilizers were dissolved in 250 ml of

**Table 1**  
Chemical compositions of dried silica gels (in terms of oxides) by XRF.

$\text{Na}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{SO}_3$	Cl	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$
0.33	0.36	97.71	0.10	0.50	0.86	0.03

deionized water with continuous stirring for 3min, and the pH values of the solutions after standing for 15min were measured by the pH meter (S40k, Mettler Toledo, Zurich, Switzerland).

### 3. Results and discussions

Silicate fertilizers were prepared by pulping the silica gels with added CaO or MgO according to the (Ca + Mg)/Si molar ratios. The active silica contents of silicate fertilizers were measured by ICP and colorimetric methods for comparisons and validations, and the pH values were measured by the pH meter. Both the active silica contents and the pH values of silicate fertilizers could be related to the chemical compositions of silicate fertilizers, with the four regions identified. The phases of silicate fertilizers were characterized by XRD with varying the (Ca + Mg)/Si molar ratios. The XRF, XRD, and pH measurements were also used to investigate the commercial slag silicate fertilizers, and the results were compared with the silicate fertilizers prepared in this work.

#### 3.1. Active silica contents in silicate fertilizers with varying the Ca/Si molar ratios

The silica gels were precipitated and separated from the acid deashing solutions of coals, and silicate fertilizers were prepared by pulping the silica gels with CaO. The chemical compositions of dried silicate fertilizers were measured by XRF for the calculation of the Ca/Si molar ratios. The measured active silica contents in relation to the Ca/Si molar ratios were given in Fig. 2.

Generally, the curve of the active silica contents versus the Ca/Si molar ratios could be divided into the four regions, as measured and validated by ICP and colorimetric methods. Prior to the Ca/Si molar ratio of  $\sim 1.50$  in Region I, the active silica content ascends sharply with increasing the Ca/Si molar ratio. As the active silica content peaks at the Ca/Si molar ratio of  $\sim 1.50$ , it descends rapidly till the Ca/Si molar ratio of  $\sim 2.25$  in Region II. Then, the active silica content descends gently till Ca/Si molar ratio of  $\sim 3.50$  in Region III. With increasing the Ca/Si molar ratio to higher values, the active silica descends even slower in Region IV. The dash line in Fig. 2 corresponds to the active silica content of 20 %, which has been set as the lower limit of quality silicate fertilizer according to the China Standard NY/T 797–2004 “Silicate Fertilizer”. Therefore, quality silicate fertilizers could be prepared in the Ca/Si molar ratios from  $\sim 1.10$  to  $\sim 3.50$ .

For the active silica contents of silicate fertilizers measured by ICP and colorimetric methods, some differences occur in Fig. 2. Generally, the active silica contents by colorimetric method could be 1–2% lower than those by ICP method. Because ICP has been used as the standard for silicon measurement, the underestimations should be ascribed to the formation of polysilicic acid unaccounted by colorimetric method [19,20]. Large differences usually occur in Regions I and II, which can reach over 4 % at the Ca/Si molar ratio of  $\sim 1.50$ . In these two regions, the active silica contents change sharply with varying the Ca/Si molar ratio, even small shifts in the Ca/Si molar ratios can cause large response in the active silica content. Moreover, more concentrated silicon in Regions I and II would allow for the formation of more polysilicic acid.

#### 3.2. pH values of the silicate fertilizers with varying the Ca/Si molar ratios

Due to the general chemical compositions, slag silicate fertilizers should be highly alkaline. The pH values of slag silicate fertilizers could be 9.9–12.3 [2], 11.99 [21], or 13.96 [8], and the application of slag silicate fertilizer in agriculture would increase the pH values of soils [8,21]. The pH values of silicate fertilizers were measured according to China Standard NY/T 1973–2010 “Water soluble fertilizers-Determination of water insoluble matter content and pH”, and the results are given in Fig. 3.

Similar to the curve of the active silica contents versus the Ca/Si molar ratios in Fig. 2, four regions can also be marked for the curve of the pH values versus the Ca/Si molar ratios in Fig. 3. In Region I, the pH value ascends rapidly with the increase of the Ca/Si molar

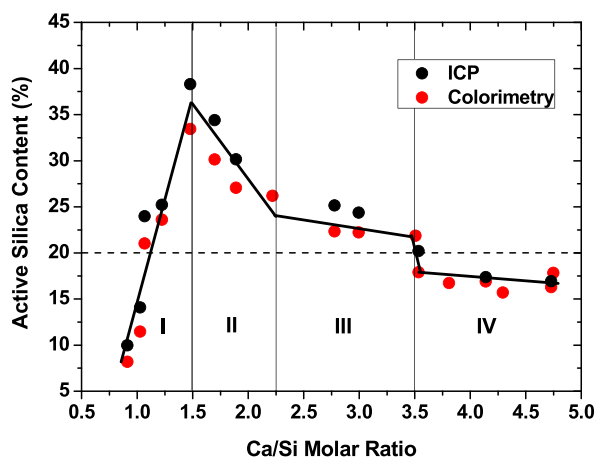


Fig. 2. Active silica contents in percentage (%) in the silicate fertilizers with varying the Ca/Si molar ratios, measured by both ICP and colorimetric methods.

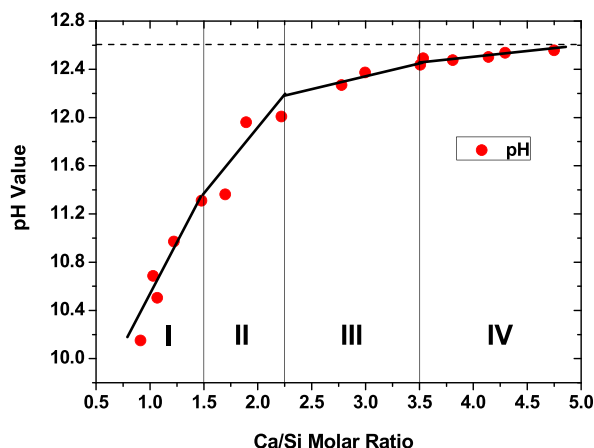


Fig. 3. pH values of the silicate fertilizers with varying the Ca/Si molar ratios.

ratio, reaching  $\sim 11.3$  at the Ca/Si molar ratio of 1.50. In Regions II, III and IV, the pH value ascends in decreasing rates, and reaches finally the pH value of  $\sim 12.6$ , the very pH value for saturated  $\text{Ca}(\text{OH})_2$  solutions. By referring to Fig. 2, it can be seen that, the highest active content occurs at the pH value of  $\sim 11.30$  with the Ca/Si molar ratio of  $\sim 1.50$ . By comparison, the measured pH value of the commercial silicate fertilizer was 10.90 with the Ca/Si molar ratio of 1.69.

### 3.3. Phase identifications of the silicate fertilizers with varying the (Ca + Mg)/Si molar ratios by XRD

With the active silica contents and pH values being measured, it is appropriate to investigate silicate fertilizers by XRD, so that the molecular structures for physicochemical properties could be explored. Representing Regions I, II, III and IV, the four silicate fertilizers with the Ca/Si molar ratios of 0.91, 1.70, 3.00 and 4.14 were selected for XRD investigations, and the diagrams are given in Fig. 4, together with the XRD diagram of dried silica gels in the bottom.

The dried silica gels with the measured active silica content of 1.37 % displays a wide envelope centered at  $\sim 23.1^\circ$ , corresponding to amorphous silica (PDF# 29-0085). For the silicate fertilizers with the Ca/Si molar ratio of 0.91 in Region 1, the small peak at  $\sim 16.7^\circ$  can be ascribed to the water-insoluble  $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$  (PDF# 34-0002), and the three peaks at  $\sim 29.5^\circ$ ,  $\sim 32.1^\circ$  and  $\sim 50.0^\circ$  ascribed to the water-insoluble  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  (PDF# 33-0306). With increasing the Ca/Si molar ratio to 1.70 in Region II, the peak at  $\sim 16.7^\circ$  becomes much weakened, indicating  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  would be preferably formed relative to  $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ . With increasing the Ca/Si molar ratio to 3.00 in Region III,  $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$  becomes disappeared and  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  still remains in silicate fertilizers, and  $\text{Ca}(\text{OH})_2$  (PDF# 44-1481) occurs with ten new peaks at  $\sim 18.0^\circ$ ,  $\sim 28.5^\circ$ ,  $\sim 34.2^\circ$ ,  $\sim 47.1^\circ$ ,  $\sim 50.5^\circ$ ,  $\sim 54.4^\circ$ ,  $\sim 62.6^\circ$ ,  $\sim 64.2^\circ$ ,  $\sim 71.8^\circ$  and  $\sim 84.8^\circ$ . With increasing the Ca/Si molar ratio to 4.14 in Region IV, the peaks for  $\text{Ca}(\text{OH})_2$  grow stronger relative to those for  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$ .

It has been found that MgO was not as effective as CaO in the preparation of silicate fertilizers. Addition of MgO in the silica gels by the Mg/Si molar ratio of 1.27 would yield the silicate fertilizers with the measured active silica content of 16.98 %. By contrast, the

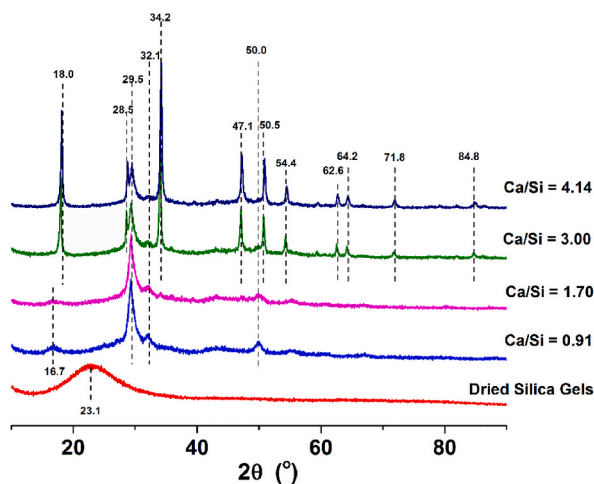


Fig. 4. XRD diagrams of the silicate fertilizers with varying the Ca/Si molar ratios.

silicate fertilizers with similar Ca/Si molar ratios could have active silica contents of  $\sim 30\%$  by referring to Fig. 2. To investigate further the effects of MgO and CaO additions on the active silica contents, more silicate fertilizers were prepared by varying the (Ca + Mg)/Si molar ratios, the active silica contents were measured, and the phases were investigated by XRD, as shown in Fig. 5. For the silicate fertilizer with the Mg/Si molar ratio of 1.27, the water-insoluble  $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$  (PDF# 01–0094) appears with the five peaks at  $20.4^\circ$ ,  $25.0^\circ$ ,  $35.3^\circ$ ,  $43.0^\circ$  and  $59.7^\circ$ . With decreasing the Mg/Si molar ratio to 0.93 and increasing the Ca/Si molar ratio to 0.66, the measured active silica content was 15.45 %, the five peaks for  $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$  become largely weakened, and  $1.5\text{CaO}\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}$  occurs with the three peaks at  $\sim 29.5^\circ$ ,  $\sim 32.1^\circ$  and  $\sim 50.0^\circ$ . With decreasing the Mg/Si molar ratio to 0.24 and increasing the Ca/Si molar ratio to 1.38, the measured active silica content increased to 20.68 %, the five peaks for  $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$  become almost invisible, and the three peaks for  $1.5\text{CaO}\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}$  grow even stronger. With basically stabilizing the Mg/Si molar ratio (0.27 this time) and increasing the Ca/Si molar ratio to 1.66, and the measured active silica content increased to 26.57 %, the five peaks for  $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$  totally disappears and the three peaks for  $1.5\text{CaO}\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}$  still remains, the water-insoluble  $\text{Mg}(\text{OH})_2$  (PDF# 44–1482) occurs with four new peaks at  $\sim 18.5^\circ$ ,  $\sim 37.8^\circ$ ,  $\sim 50.7^\circ$  and  $58.3^\circ$ . Therefore, the silica gels would prefer to react with CaO, and the MgO would be left for hydrolysis if CaO is enough in the silicate fertilizers.

### 3.4. Phase identifications in the commercial slag silicate fertilizers

Due to the treatments by high temperatures, slag silicate fertilizers could be very complicated in nature. However, little work has been made on the chemical compositions and phase identifications of slag silicate fertilizers. The steel slags from Taiyuan Iron and Steel (Group) Co., Ltd., Taiyuan, Shanxi [8], composed of CaO (51.84 %), FeO (6.17 %),  $\text{Al}_2\text{O}_3$  (4.39 %), MgO (9.74 %), MnO (0.29 %), S (0.18 %),  $\text{SiO}_2$  (28.20 %), and  $\text{TiO}_2$  (0.35 %), have been previously used for the co-remediation of cadmium-polluted soils. No information was given of the active silica content and phases for the steel slags. The silica gels in this work are of high purity, and the silicate fertilizers prepared by adding CaO or MgO in the silica gels can thus act as model fertilizers, which would provide some insights into the commercial slag silicate fertilizers. The detailed chemical compositions of the selected commercial slag silicate fertilizers (Slag Fertilizer) and the silicate fertilizers (Fertilizer 1 and Fertilizer 2) prepared in this work are given in Table 2. Generally, the active silica contents of silicate fertilizers should be lower than the  $\text{SiO}_2$  contents, due to the partial dissolution of silica in 0.5 M HCl solutions. Fertilizer 1 and Fertilizer 2 could be ideally chosen as the model fertilizers in this work for phase investigations due to their similar Ca/Si and Mg/Si ratios with Slag Fertilizer, which were supposed to form similar phases. Slag Fertilizer with measured pH value of 10.90 and active silica content of 30.53 % (by ICP) was found to have very similar chemical compositions with the steel slags discussed above, especially for CaO (50.41 %) and  $\text{SiO}_2$  (31.94 %). By comparison, Fertilizer 1 prepared with the addition of CaO in this work was mainly composed of CaO (60.50 %) and  $\text{SiO}_2$  (38.17 %), and the pH value was  $\sim 11.40$  by referring to Fig. 3. The higher pH value for Fertilizer 1 could be due to the higher CaO content. Fertilizer 2 was prepared by adding CaO and MgO in the silica gels, and the Ca/Si and Mg/Si ratios were very close to those for Slag Fertilizer in Table 2.

The XRD diagrams of Fertilizer 1, Fertilizer 2, and Slag Fertilizer are displayed in Fig. 6. As discussed in the previous sections, the three peaks at  $\sim 29.5^\circ$ ,  $\sim 32.1^\circ$  and  $\sim 50.0^\circ$  should be ascribed to  $1.5\text{CaO}\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}$  (PDF# 33–0306), the four peaks at  $\sim 18.5^\circ$ ,  $\sim 37.8^\circ$ ,  $\sim 50.7^\circ$  and  $58.3^\circ$  should be ascribed to  $\text{Mg}(\text{OH})_2$  (PDF# 44–1482), and the small peak at  $\sim 16.7^\circ$  should be ascribed to  $\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$  (PDF# 34–0002). By comparisons with Fertilizer 1 and Fertilizer 2 prepared in this work, the peaks for  $\text{Mg}(\text{OH})_2$  and  $\text{CaO}\cdot \text{SiO}_2\cdot \text{H}_2\text{O}$  do not appear in Slag Fertilizer. Surprisingly, the two main sharp peaks at  $\sim 29.5^\circ$  and  $\sim 32.1^\circ$  stand clearly above the big envelope of amorphous glasses, which could be attributed to  $1.5\text{CaO}\cdot \text{SiO}_2\cdot x\text{H}_2\text{O}$  with the third peak appearing at  $\sim 50.0^\circ$  in the XRD diagram of Slag Fertilizer. It has been generally known that the molten slags would be quenched by water to prepare slag silicate fertilizers. Therefore, the molten slags would be mostly frozen as amorphous glasses during the water-cooled process, which can be

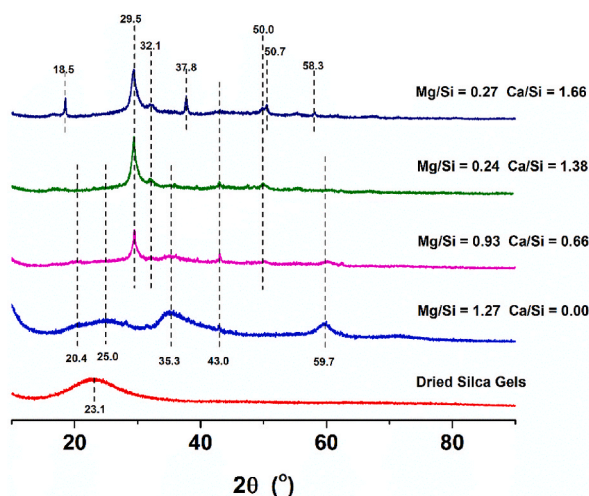


Fig. 5. XRD diagram of the silicate fertilizers with varying the (Ca + Mg)/Si molar ratios.

**Table 2**

Chemical compositions (in oxides) by XRF of the commercial slag silicate fertilizers (Slag Fertilizer) and the silicate fertilizers (Fertilizer 1 and Fertilizer 2) prepared in this work.

Sample	Ca/Si	Mg/Si	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Slag Fertilizer	1.69	0.26	0.25	5.45	7.82	31.94	2.41	0.51	50.41	0.54	0.44
Fertilizer 1	1.70	0.02		0.47	0.22	38.17	0.09	0.01	60.50	0.36	0.09
Fertilizer 2	1.66	0.27		6.51	0.19	36.29	0.09	0.00	56.29	0.42	0.06

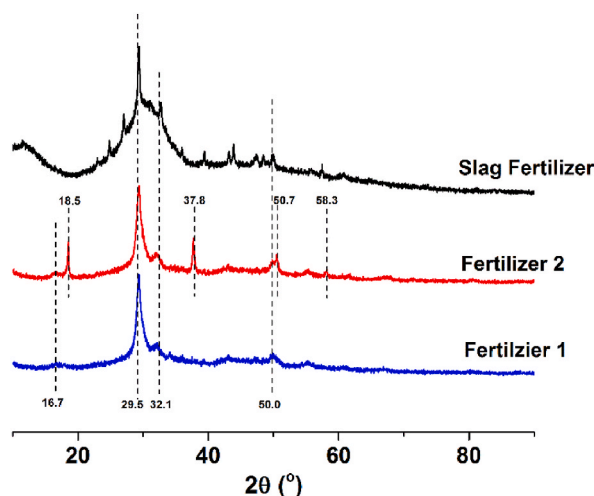


Fig. 6. XRD diagrams of Fertilizer 1, Fertilizer 2, and Slag Fertilizer in Table 2.

approved by the big envelope in the XRD diagram of Slag Fertilizer. Nevertheless,  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  would also crystallize from the amorphous glasses because cooling could not be evenly applied. Because the big envelope extends mainly around the two main sharp peaks at  $\sim 29.5^\circ$  and  $\sim 32.1^\circ$  attributed to  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$ , amorphous glasses would probably have the same chemical compositions. Therefore, Slag Fertilizer should be mainly composed of  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  in crystalline and amorphous states. Complicated crystals could have been formed by MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SO<sub>3</sub> in small quantities according to Table 2 during water-cooled process, which could account for the many small sharp peaks scattered in the XRD diagram of Slag Fertilizer.

#### 4. Conclusions

The importance of silicon for plants has been well established, and the depletion of silicon in soils due to agriculture would endanger the yields and growth of plants. Despite many raw materials and activation methods being used for the preparation of silicate fertilizers, the most common silicate fertilizers could be slags, but the production has been very limited due to heavy metals. Recently, the silicate fertilizers have been produced with little heavy metals by using fly ashes after alumina extractions, but the sodium added or left could cause new problems in long term applications.

In this work, coals were deashed to obtain the acid deashing solutions, in which the silica gels of high purity could be precipitated with little heavy metals by driving off excessive water and acid. After separation by pressure filtering, the silica gels should be of high reactivity. By pulping the silica gels with CaO under mild conditions, new silicate fertilizers have been prepared without sodium. The active silica contents of silicate fertilizers with varying the Ca/Si molar ratios were measured and validated by ICP and colorimetric methods. Four regions could be marked in the curve of the active silica contents versus the Ca/Si molar ratios, and quality silicate fertilizers occurred in the Ca/Si molar ratios from  $\sim 1.10$  to  $\sim 3.50$ . The pH values of silicate fertilizers were measured and could also be related to the four regions, and the highest active silica content occurred at the pH value of  $\sim 11.30$  with the Ca/Si molar ratio of  $\sim 1.50$ . Silicate fertilizers selected from the four regions were investigated by XRD, and the water-insoluble  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  was identified as the contributor of active silica in the silicate fertilizers. For the silicate fertilizers prepared with CaO fully or partially replaced by MgO, the silica gels would preferably react with CaO, and the active silica contents grew with the increase of CaO. Due to the simple chemical compositions and clearly identified phases, the silicate fertilizers prepared in this work could act as the perfect models. By referring to the model silicate fertilizers prepared by varying the (Ca + Mg)/Si ratios,  $1.5\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$  in crystalline and amorphous states was confirmed as the dominant in one commercial slag silicate fertilizer. This work could have made the first report of detailed chemical compositions and phases for the contributors of active silica in silicate fertilizers.

Quality silicate fertilizers made in this work should be integrated with the chemical deashing of coals. In the chemical deashing of coals, the ultraclean coals with low ashes should be the main product, which can be used for making advanced carbon materials [16, 17], ensuring the good profit for the coal deashing. At the same time, the deashing solutions of coals would be contaminated by coal

ash elements, causing environmental problems and necessitating regeneration of chemicals. Development of quality silicate fertilizers from the deashing solutions of coals can help to mitigate secondary pollution and reduce the cost of coal deashing by chemical regeneration.

#### Data availability statement

No data was used for the research described in the article.

#### CRediT authorship contribution statement

**Lijun Zhao:** Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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