TECHNICAL ARTICLE

Comparative study of the isothermal solid-state reaction systems of kaolinite–Na$_2$CO$_3$ and kaolinite–quartz–Na$_2$CO$_3$ for coal gangue activation

Kezhou Yan [ORCID],[a)] Yaru Guo, Yuanyuan Zhang, Yanxia Guo, and Fangqin Cheng
State Environmental Protection Key Laboratory on Efficient Resource-Utilization Techniques of Coal Waste, Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, China

A clear understanding of the solid-state reaction of kaolinite (Kln), quartz (Qtz), and sodium carbonate (Na$_2$CO$_3$) is of great significance for the process optimization of coal gangue calcined with Na$_2$CO$_3$. In this work, a comparative study of the isothermal solid-state reaction systems of Kln–Na$_2$CO$_3$ and Kln–Qtz–Na$_2$CO$_3$ was performed by means of X-ray diffraction (XRD), scanning electron microscope, and energy dispersion spectroscopy (SEM-EDS). The results showed that the calcined products both for these reaction systems mainly contain different kinds of sodium aluminum silicates (e.g., NaAlSiO$_4$, Na$_{1.55}$Al$_{1.55}$Si$_{0.45}$O$_4$, and Na$_{1.95}$Al$_{1.95}$Si$_{0.05}$O$_4$) and various kinds of sodium silicates (e.g., Na$_2$Si$_3$O$_7$, Na$_2$SiO$_3$, and Na$_6$Si$_2$O$_7$). The mass percentage of Na$_2$CO$_3$ played a key role in the phase transformation, determining the Na/Al/Si molar ratio of the formed sodium aluminum silicates. Compared with the reaction system of Kln–Na$_2$CO$_3$, the existence of Qtz inhibited the formation of sodium aluminum silicates in the reaction system of Kln–Qtz–Na$_2$CO$_3$. It should be noted that the formed phases both for these reaction systems were slightly different from that of the thermodynamical calculated results of Na$_2$O–SiO$_2$–Al$_2$O$_3$ using FactSage™ software. According to both the experimental and calculated results, a reasonable batching area for coal gangue activation was proposed that the addition of Na$_2$CO$_3$ should be in the range of 20–50% of the total mass of Kln, Qtz, and Na$_2$CO$_3$. © The Author(s), 2022. Published by Cambridge University Press on behalf of International Centre for Diffraction Data. [doi:10.1017/S0885715622000434]

Key words: kaolinite, quartz, sodium carbonate, isothermal calcination, XRD analysis, phase transformation

I. INTRODUCTION

Coal gangue produced from coal mining and coal processing is one of the largest amounts of industrial solid wastes in China. It is obviously necessary to achieve greater resource utilization of coal gangue, in order to solve the ecological and environmental problems caused by its accumulation (Yang *et al.*, 2012; Yu *et al.*, 2012; Ji *et al.*, 2014; Lü *et al.*, 2014; Guo *et al.*, 2016; Yan *et al.*, 2016). Recently, the extraction of alumina from coal gangue has attracted many researchers' attention since it contains 15–40% wt.% alumina (Cheng *et al.*, 2012; Ji *et al.*, 2014; Xiao *et al.*, 2015; Guo *et al.*, 2016). The major aluminum-containing mineral in coal gangue is kaolinite (Kln) with low reactivity, which leads to a low alumina extraction by the direct leaching method (Vassilev and Vassileva, 1996; Jabłońska, 2012; Yan *et al.*, 2016). Thus, it is of great importance to activate the reactivity of coal gangue before the leaching process (Hu *et al.*, 2008; Chao *et al.*, 2010; Cheng *et al.*, 2012; Guo *et al.*, 2014a, 2016; Liu *et al.*, 2014; Xiao *et al.*, 2015). Many studies show that coal gangue calcined with sodium carbonate (Na$_2$CO$_3$) would transform the aluminum-containing minerals into sodium aluminum silicates, which presents a high dissolution of aluminum in acid (Hu *et al.*, 2008; Guo *et al.*, 2014a; Liu *et al.*, 2014).

Meanwhile, the acid-leaching residue would be presented in the form of amorphous silica, which is beneficial to its further resource utilization (Hu *et al.*, 2008; Guo *et al.*, 2014a). However, a difficult problem is the excessive consumption of Na$_2$CO$_3$. A clear understanding of the activation mechanism of coal gangue calcined with Na$_2$CO$_3$ is of great significance for the further process optimization.

To date, many researches have been devoted to reveal the reaction mechanism of coal gangue calcined with Na$_2$CO$_3$ (Hu *et al.*, 2008; Guo *et al.*, 2014a; Liu *et al.*, 2014). In these works, a series of sodium aluminum silicates such as nepheline (hexagonal, NaAlSiO$_4$) and zeolite (cubic, NaAlSiO$_4$) were detected and considered as the target phases for the coal gangue calcined with Na$_2$CO$_3$. Meanwhile, some aluminum-free phases such as sodium trisilicate (orthorhombic, Na$_2$Si$_3$O$_7$) and sodium metasilicate (hexagonal, Na$_2$SiO$_3$) were also formed, which leaded to an additional consumption of Na$_2$CO$_3$ (Hu *et al.*, 2008; Guo *et al.*, 2014a; Liu *et al.*, 2014). A controlling of the formation of these aluminum-free sodium silicates is apparently necessary in order to achieve a reduction of Na$_2$CO$_3$ consumption. Actually, the phase composition of the calcined product is associated with the mineral composition of coal gangue used and the amount of Na$_2$CO$_3$ added. The main minerals in coal gangue are kaolinite (Kln) and quartz (Qtz), which account for about 10–70% and 15–35%, respectively (Shi *et al.*, 2008; Guo *et al.*, 2014b; Zhang *et al.*, 2015).

a)Author to whom correspondence should be addressed. Electronic mail: yankz@sxu.edu.cn

The reaction mechanism of Kln calcined with Na_2CO_3 has been extensively investigated (Kubo *et al.*, 1966, 1967, 1968; Yan *et al.*, 2017). Kubo *et al.* (1966, 1967, 1968) studied the solid-state reaction between Kln and Na_2CO_3 within 600–1400 °C and found that Kln decomposed at about 600 °C and transformed to low-temperature carnegieite, nepheline and high-temperature carnegieite in turn at 700, 800–850, and 1270 °C, respectively. In our recent work, we proposed a reaction mechanism of Kln calcined with Na_2CO_3 at 400–900 °C and found that all the obtained sodium aluminum silicates mainly consist of anion frame-like structures with alternating connection of $[AlO_4]$ and $[SiO_4]$ (Yan *et al.*, 2017). These studies investigated the phase transformation of Kln calcined with Na_2CO_3 at different temperatures in detail, but the phase transformation of Kln calcined with different amounts of Na_2CO_3 at a certain temperature, for instance, 850 °C, which is the appropriate temperature of coal gangue activated with Na_2CO_3, is still not clear. On the other hand, quartz (Qtz) as one of the main aluminum-free minerals would affect the reaction process undoubtedly. The related understanding is of great importance for further revealing the activation mechanism of coal gangue calcined with Na_2CO_3. Up to now, few studies have been reported. A closely related report is about the ternary phase diagram of $Na_2O–SiO_2–Al_2O_3$, which was reported in detail by Schairer and Bowen (1956), and then the available thermodynamic and phase data were calculated by Guillaume and Patrice using the FactSage™ thermochemical software (Lambotte and Chartrand, 2013). However, these results could be only used as a preliminary guide to estimate the phase composition of the products, since the differences between metallic oxides and specific minerals exist in objective reality.

In this work, a comparative study of the isothermal solid-state reaction systems of Kln–Na_2CO_3 and Kln–Qtz–Na_2CO_3 at 850 °C was performed in detail. The calculated data about the phase diagram of $Na_2O–SiO_2–Al_2O_3$ using FactSage™ software were also compared with the experimental results obtained from this work. Besides, the all above results were used to control the formation of aluminum-free sodium silicates, and further reduce the consumption of Na_2CO_3 during the coal gangue activation.

II. EXPERIMENTAL

A. Materials

Kaolinite used in this study was purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing. The chemical composition and loss on ignition (LOI) are shown in Table I. In addition, both the quartz and Na_2CO_3 samples used in this work were analytical reagents purchased from Beichen Chemical Reagent Factory, Tianjin.

B. Methods

A series of mixtures with various mass percentages were prepared in order to systematically investigate the phase transformation in the isothermal solid-state reaction systems of Kln–Na_2CO_3 and Kln–Qtz–Na_2CO_3. The mass percentages of individual components and sample codes are given in Figure 1. The initial reactant mixtures were respectively placed in a platinum crucible, and heated in a muffle furnace (SX2-12-10, Shanghai Hongji Instrument Co. Ltd., China) under identical conditions. Here, the calcination temperature and calcination time were set at 850 °C and 180 min, respectively, in order to keep consistent with the optimized reaction conditions of coal gangue calcined with Na_2CO_3 (Hu *et al.*, 2008; Guo *et al.*, 2014a; Liu *et al.*, 2014). After calcination, the obtained samples were cooled to room temperature in a desiccator and then ground into powder in an agate mortar.

C. Characterization

The phase compositions of the calcined products were identified using X-ray diffraction (XRD) spectrometer (BRUKER, PHASERD 2) equipped with a Cu$K\alpha$ radiation and an advanced linear detector (LYNXEYE). The acceleration voltage and electrical current were 30 kV and 10 mA, respectively. The scans were performed from 5° to 60° with a 0.01° step size and a counting time of 0.1 s step^{-1}.

The morphology and elemental analysis of each sample were examined by a field-emission scanning electron microscope (SEM; FESEM JSM-7001F) equipped with an X-ray energy-dispersive spectrometer (EDS; SwiftED, Oxford, UK). The samples were mounted on an aluminum stab by using a double-sided adhesive tape and then coated with 200 Å of gold in an ion coater unit under 10–50 mm of vacuum. All measurements were performed with a 20 kV accelerating voltage and a micrometer-sized electron beam scanned over a sample surface area of approximately 1 mm^2.

D. FactSage™ thermodynamic calculation

Thermodynamic calculation of the phase diagram of $Na_2O–Al_2O_3–SiO_2$ was executed using FactSage™ software in this work. During the calculation process, the self-established database was firstly created according to the thermodynamic and phase equilibrium data from the basic database of FactSage™ software; the self-established database was introduced in the Phase Diagram to obtain the isothermal phase diagram of $Na_2O–Al_2O_3–SiO_2$ at 850 °C; then the resulting phase diagram was automatically plotted by the Figure Module. The detailed operation procedures about this thermodynamic software were described elsewhere (Lambotte and Chartrand, 2013).

TABLE I. Chemical compositions and loss on ignition of the as-received kaolinite.

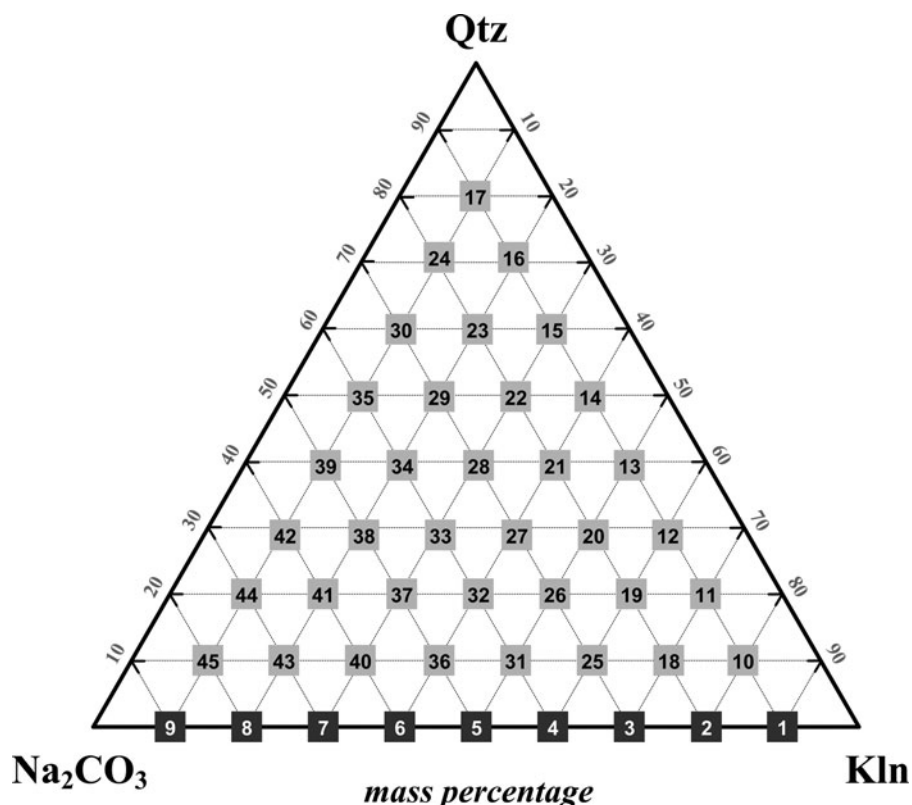| Components	SiO$_2$	Al$_2$O$_3$	TiO$_2$	Na$_2$O	CaO	MgO	K$_2$O	Fe$_2$O$_3$	LOIa
Contents (wt.%)	45.71	35.95	0.73	0.60	0.57	0.33	0.29	0.16	15.66

[a]LOI denoted the loss on ignition at 850 °C.

Figure 1. Sample codes based on the mass percentages of Kln, Qtz, and Na_2CO_3. (XRD patterns for each specimen in Supplementary material).

III. RESULTS

A. Phase transformation of Kln–Na_2CO_3 quasi-binary system calcined at 850 °C

Phase transformation of Kln–Na_2CO_3 quasi-binary system calcined at 850 °C was investigated firstly, since Kln was the main aluminum-containing mineral in coal gangue. The XRD patterns of Kln–Na_2CO_3 quasi-binary system calcined at 850 °C are displayed in Supplementary Figure S2 (*No.* 1–9) and the results are summarized in Table II, where "✓" indicates that the phase is detectable in the calcined products. The results showed that the formed aluminum-containing phases mainly included low-temperature carnegieite (L-phase, orthorhombic, $NaAlSiO_4$), nepheline (Nph, hexagonal, $NaAlSiO_4$), zeolite (Zeo, cubic, $NaAlSiO_4$), sodium aluminum silicate-1 (SAS-1, orthorhombic, $Na_{1.55}Al_{1.55}Si_{0.45}O_4$), and sodium aluminum silicate-2 (SAS-2, tetragonal, $Na_{1.95}Al_{1.95}Si_{0.05}O_4$). In addition, the calcined products from this reaction system also contained some other aluminum-free phases, such as sodium trisilicate (S_t, orthorhombic, $Na_2Si_3O_7$), sodium metasilicate (S_m, hexagonal, Na_2SiO_3), and sodium pyrosilicate (S_p, monoclinic, $Na_6Si_2O_7$).

As shown in Table II and Figure 2, the mass percentage of Na_2CO_3 in the initial reactant mixture had an obvious effect on the phase composition of the calcined product. When the mass percentage of Na_2CO_3 was <30%, the formed sodium aluminum silicates included L-phase, Nph, and Zeo. The molar ratio of Na, Al, and Si in these phases all were 1:1:1. With the mass percentage of Na_2CO_3 increased to 40–50%, another sodium aluminum silicate, SAS-1, with a high molar ratio of Al/Si (1.55:0.45) formed. Here, it should be noted that the Na/Si

and Al/Si molar ratios were always equal to each other in order to maintain the charge neutrality and structural stability of the calcined products (Yan *et al.*, 2017). Further increasing the mass percentage of Na_2CO_3 to >60%, the formed sodium aluminum silicate was only the SAS-2 with a higher Al/Si molar ratio (1.95:0.05). It suggested that the Al/Si molar ratio of sodium aluminum silicate in the calcined product gradually increased with the increasing of the mass percentage of Na_2CO_3. For the aluminum-free phases, there were $Na_2Si_3O_7$ (S_t), Na_2SiO_3 (S_m), and $Na_6Si_2O_7$ (S_p) in the calcined products when the mass percentage of Na_2CO_3 was >40%. In addition, the Qtz and Na_2CO_3 could be detected in the calcined products when the mass percentages of Na_2CO_3 were <20% and >80%, respectively, which should be the unreacted phases from the initial reactant mixture.

SEM-EDS analysis was performed in order to further clarify the reaction between Kln and Na_2CO_3 at 850 °C. As shown in Figure 3, the calcined samples obtained from the mixtures with the mass percentage of $Na_2CO_3 < 30\%$ (Samples *NO*. 2 and 3) presented the morphology of fine irregular particles. EDS analysis showed that the Na, Al, and Si elements uniformly distributed in the surface for these samples. It was consistent with the results of XRD analysis that the aluminum-containing phases with the Na/Al/Si molar ratio of 1:1:1 formed in the calcined products. When the mass percentage of Na_2CO_3 was >50% (Sample *NO*. 5, 6, and 8), the powder particles fused and displayed in the form of the irregular glass melts. Particularly, it could be found that the particle size and melting degree were obviously increased with the increasing of the mass percentage of Na_2CO_3. Meanwhile,

TABLE II. Phase compositions of Kln–Na$_2$CO$_3$ quasi-binary system calcined at 850 °C.

	Mass percentages (%)		Sodium aluminum silicates					Aluminum-free phases				
No.	Na$_2$CO$_3$	Kln	L-phase NaAlSiO$_4$ Orthorhombic 96-101-0958	Nph NaAlSiO$_4$ Hexagonal 96-100-8762	Zeo NaAlSiO$_4$ Cubic 01-192-6489	SAS-1 Na$_{1.55}$Al$_{1.55}$Si$_{0.45}$O$_4$ Orthorhombic 96-200-2895	SAS-2 Na$_{1.95}$Al$_{1.95}$Si$_{0.05}$O$_4$ Tetragonal 96-200-2892	S$_t$ Na$_2$Si$_3$O$_7$ Orthorhombic 01-164-1293	S$_m$ Na$_2$SiO$_3$ Hexagonal 00-016-0818	S$_p$ Na$_6$Si$_2$O$_7$ Monoclinic 00-027-0784	Qtz SiO$_2$ Hexagonal 01-167-0146	Na Na$_2$CO$_3$ Monoclinic 01-164-1148
1	10	90	✓								✓	
2	20	80	✓								✓	
3	30	70		✓								
4	40	60		✓	✓							
5	50	50			✓	✓		✓				
6	60	40				✓	✓	✓	✓	✓		
7	70	30					✓		✓	✓		
8	80	20					✓		✓	✓		✓
9	90	10					✓			✓		✓

NOTE 1: L-phase, Low-temperature carnegieite; Nph, Nepheline; Zeo, Zeolite; SAS-1, Sodium aluminum silicate-1; SAS-2, Sodium aluminum silicate-2; S$_t$, Sodium trisilicate; S$_m$, Sodium metasilicate; S$_p$, Sodium pyrosilicate; Qtz, Quartz; Na, Sodium carbonate.

NOTE 2: ✓ indicates that the phase was observed by XRD in mixture after calcining at 850 °C.

the Na, Al, and Si element distribution displayed an obvious segregation. There were a series of characteristic regions with aluminum-rich but silicon-deficit (marked with the white square in Figure 3), which was consistent with the XRD results that Na$_2$Si$_3$O$_7$, Na$_2$SiO$_3$, or Na$_6$Si$_2$O$_7$ were formed when the mass percentages of Na$_2$CO$_3$ was >50%. The formation of these sodium silicates made the powder particles melt and adhere together (Gibsont and Ward, 2010). In addition, the segregation of sodium silicates also implied that the formed sodium aluminum silicates in the calcined samples would have a characteristic of the Al/Si ratio beyond 1, since the Al/Si ratio was near to 1 in the initial reactant mixtures.

B. Phase transformation of Kln–Qtz–Na$_2$CO$_3$ quasi-ternary system calcined at 850 °C

Quartz (Qtz) is the main aluminum-free minerals in coal gangue, accounting for 15–35% of the total mass. The knowledge of the reaction among Kln, Qtz, and Na$_2$CO$_3$ is also important to further understand the reaction mechanism of coal gangue calcined with Na$_2$CO$_3$. Accordingly, XRD patterns of Kln–Qtz–Na$_2$CO$_3$ quasi-ternary system calcined at 850 °C are also shown in Supplementary Figure S2 (No. 10–45) and the results are summarized in Table III. The results showed that the phase compositions of Kln–Qtz–Na$_2$CO$_3$ quasi-ternary system calcined at 850 °C were similar to that of Kln–Na$_2$CO$_3$ quasi-binary system calcined at the same temperature, as shown in Table II. The formed phases included five kinds of aluminum-containing phases (L-phase, Nph, Zeo, SAS-1, and SAS-2), and three kinds of aluminum-free phases (Na$_2$Si$_3$O$_7$ (S$_t$), Na$_2$SiO$_3$ (S$_m$), and Na$_6$Si$_2$O$_7$ (S$_p$)).

As shown in Table III, the mass percentage of Na$_2$CO$_3$ in the initial reactant mixture was still one of the most key factors, determining the phase compositions of the calcined products from the Kln–Qtz–Na$_2$CO$_3$ system. When the mass percentage of Na$_2$CO$_3$ was <20%, the calcined samples mainly consisted of L-phase. With the mass percentage of Na$_2$CO$_3$ further increasing, the other sodium aluminum silicates, such as Nph, Zeo, SAS-1, and SAS-2 formed sequentially. For example, Nph and Zeo formed from 30% of Na$_2$CO$_3$, SAS-1 from 50% of Na$_2$CO$_3$, and SAS-2 from 70% of Na$_2$CO$_3$, respectively. Here, it should be noted that the existence of Qtz would affect the reaction between Kln and Na$_2$CO$_3$. As seen from Figure 4, the addition of Qtz made the diffraction intensities of L-phase, Nph, and Zeo declined at the same mass ratio of Kln and Na$_2$CO$_3$, which indicated that the existence of Qtz inhibits the formation of L-phase, Nph, and Zeo. In particular, it should also be noted that SAS-1 and SAS-2 with a higher molar ratio of Al/Si only formed when the mass percentage of Na$_2$CO$_3$ was >50% and that of Qtz was < 30%. This indicated that the higher mass percentage of Qtz should not be favorable to the formation of these sodium aluminum silicate phases with aluminum-rich but silicon-deficit. In addition, apart from the sodium aluminum silicates mentioned above, the calcined products from the Kln–Qtz–Na$_2$CO$_3$ system also contained some other aluminum-free phases, such as Na$_2$Si$_3$O$_7$ (S$_t$), Na$_2$SiO$_3$ (S$_m$), and Na$_6$Si$_2$O$_7$ (S$_p$), when the mass percentage of Na$_2$CO$_3$ was >40%.
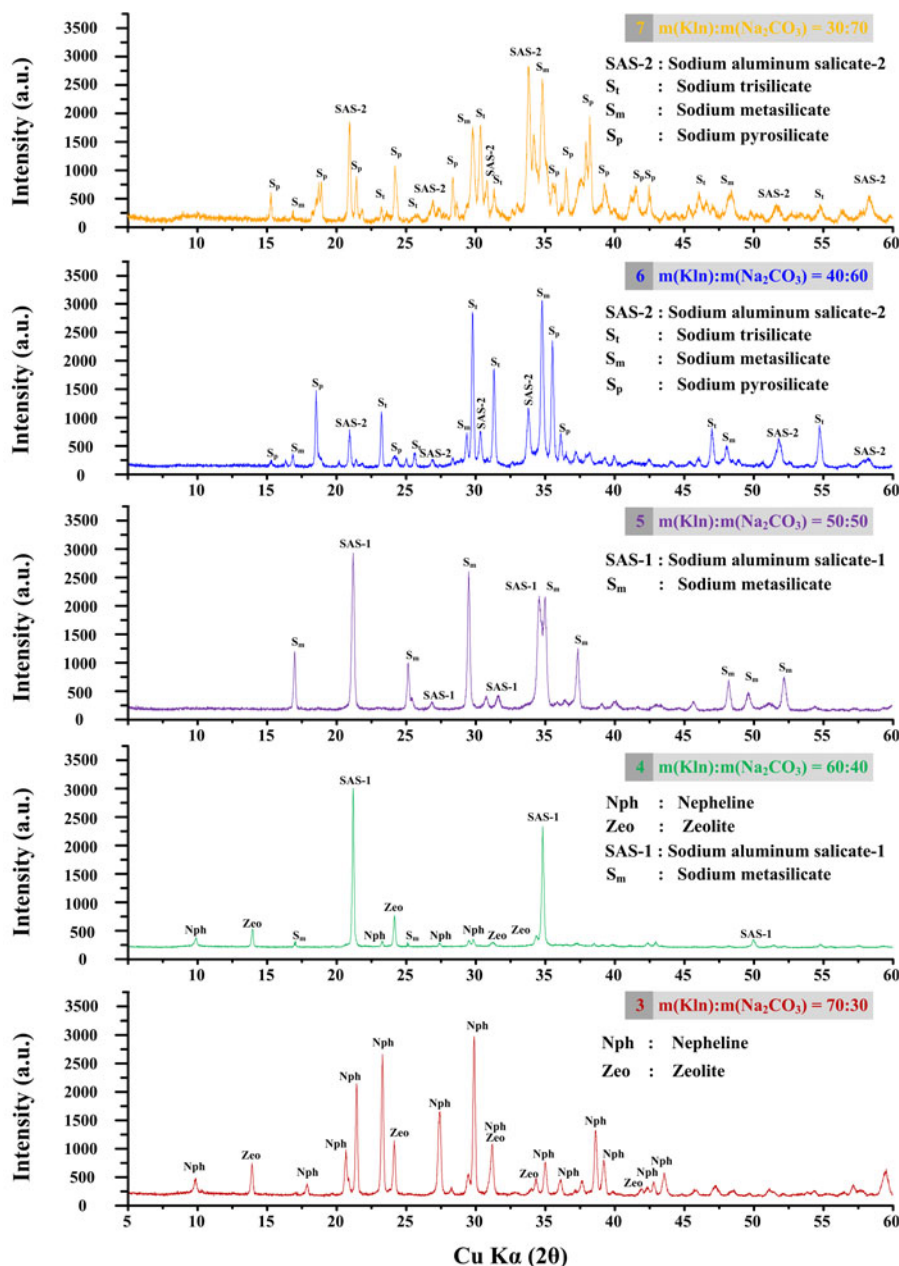
Figure 2. XRD patterns of Kln–Na$_2$CO$_3$ quasi-binary system calcined at 850 °C.

C. Thermodynamics calculation of Na$_2$O–SiO$_2$–Al$_2$O$_3$ at 850 °C

As previously mentioned, a closely related report about the phase diagram of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system has been reported in literatures (Schairer and Bowen, 1956; Lambotte and Chartrand, 2013). In this work, the isothermal section of this ternary system at 850 °C was specially calculated by the FactSage™ software (in Figure 5). It could be found that three kinds of sodium aluminates (NaAlO$_2$, Na$_2$Al$_{12}$O$_{19}$, and NaAl$_9$O$_{14}$), three kinds of sodium silicates (Na$_2$SiO$_3$, Na$_4$SiO$_4$, and Na$_6$Si$_2$O$_7$) and two kinds of sodium aluminum silicates (NaAlSi$_3$O$_8$ and NaAlSiO$_4$) were stable for the calculated results of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system at 850 °C. It was interesting to note that these formed phases were slightly different from that of the experimental results of Kln–Na$_2$CO$_3$ and Kln–Qtz–Na$_2$CO$_3$ systems at 850 °C. In particular, the

independent sodium aluminates (such as NaAlO$_2$, Na$_2$Al$_{12}$O$_{19}$, and NaAl$_9$O$_{14}$) were observed in the calculated result of Na$_2$O–Al$_2$O$_3$–SiO$_2$ system; while these phases were replaced by the sodium aluminum silicates with high Al/Si ratio such as SAS-1 (Na$_{1.55}$Al$_{1.55}$Si$_{0.45}$O$_4$) and SAS-2 (Na$_{1.95}$Al$_{1.95}$Si$_{0.05}$O$_4$) in the experimental results of Kln–Na$_2$CO$_3$ and Kln–Qtz–Na$_2$CO$_3$ systems. The main reasons for the difference between theoretical calculation and experimental measurement may be due to that (1) it is generally conducted under an ideal condition of infinite reaction time for the thermodynamic theoretical calculation, while the same operation cannot be carried out in the experimental process or industrial process; (2) the objective difference between the metallic oxides used in theoretical calculation and the specific minerals used in experimental measurement, especially that the 1:1 layered structure of Kln (a connected [AlO$_6$] layer
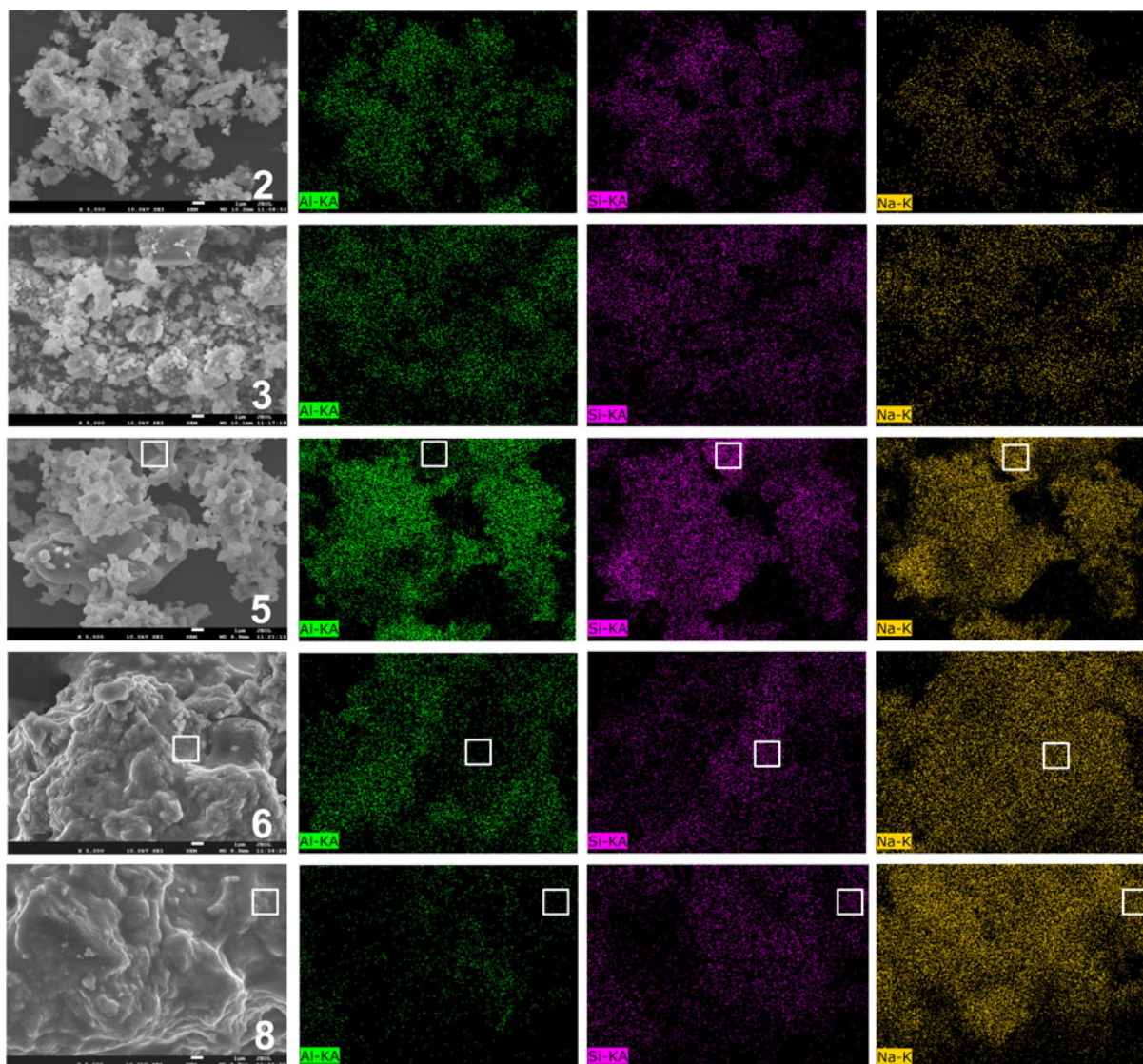
Figure 3. SEM-EDS results of Kln–Na$_2$CO$_3$ quasi-binary system calcined at 850 °C. (SEM images at 5000×).

and [SiO$_4$] layer through a shared bridging oxygen) is unfavorable to the formation of the independent sodium aluminates (Tosoni *et al.*, 2006; Guo *et al.*, 2016; Yan *et al.*, 2017).

In addition, the formed phases for the Na$_2$O–SiO$_2$–Al$_2$O$_3$ system mainly changed from tricomponent (NaAlSi$_3$O$_8$ and NaAlSiO$_4$) to bicomponent (NaAlO$_2$, Na$_2$Al$_{12}$O$_{19}$, NaAl$_9$O$_{14}$, Na$_2$SiO$_3$, Na$_6$Si$_2$O$_7$, and Na$_4$SiO$_4$) with the increase of Na$_2$O content. It was similar to the phenomenon observed in Kln–Na$_2$CO$_3$ and Kln–Qtz–Na$_2$CO$_3$ systems, where the Al/Si ratio of sodium aluminum silicate was gradually increased and the independent sodium silicates was formed with the increase of Na$_2$CO$_3$ content (Tables II and III).

IV. DISCUSSION

According to the research above, a series of sodium aluminum silicates including L-phase, Nph, Zeo, SAS-1, and SAS-2 could be detected both for the Kln–Na$_2$CO$_3$ system and the Kln–Qtz–Na$_2$CO$_3$ system calcined at 850 °C. With the exception of L-phase, all other above-mentioned phases had good solubility in acid (Guo *et al.*, 2013, 2014a) and

could be regarded as the object phases in the activation of coal gangue. Therefore, a basic requirement for the activation of coal gangue was put forward, that the mass percentage of Na$_2$CO$_3$ in the initial reactant mixture should be no less than 20%.

Although all these sodium aluminum silicates (Nph, Zeo, SAS-1, and SAS-2) had good solubility in acid, they should also be treated separately from the economical point of view. For Nph and Zeo, they both had the Na:Al:Si molar ratio of 1:1:1, namely, two moles of Al or Si would consume only one mole of Na. By contrast, SAS-1 and SAS-2 had the Na:Al:Si molar ratios of 1.55:1.55:0.45 and 1.95:1.95:0.05, respectively. Here, two moles of Al or Si would consume more than one mole of Na, which leads to an excessive consumption of Na$_2$CO$_3$. Meanwhile, it had been confirmed in Table II that the formation of SAS-1 or SAS-2 was inevitably accompanied by the formation of sodium silicates such as Na$_2$Si$_3$O$_7$, Na$_2$SiO$_3$, and Na$_6$Si$_2$O$_7$, since the Al:Si molar ratio of Kln was 1:1. Hence, no matter for the Kln–Na$_2$CO$_3$ system or the Kln–Qtz–Na$_2$CO$_3$ system calcined at 850 °C, the formation of these sodium silicates would lead to an additional consumption of Na$_2$CO$_3$.

TABLE III. Phase compositions of Kln–Qtz–Na_2CO_3 quasi-ternary system calcined at 850 °C.

No.	Mass percentages (%)			Sodium aluminum silicates					Aluminum-free phases				
	Na_2CO_3	Kln	Qtz	L-phase NaAlSiO$_4$ Orthorhombic 96-101-0958	Nph NaAlSiO$_4$ Hexagonal 96-100-8762	Zeo NaAlSiO$_4$ Cubic 01-192-6489	SAS-1 $Na_{1.55}Al_{1.55}Si_{0.45}O_4$ Orthorhombic 96-200-2895	SAS-2 $Na_{1.95}Al_{1.95}Si_{0.05}O_4$ Tetragonal 96-200-2892	S_t $Na_2Si_3O_7$ Orthorhombic 01-164-1293	S_m Na_2SiO_3 Hexagonal 00-016-0818	S_p $Na_6Si_2O_7$ Monoclinic 00-027-0784	Qtz SiO$_2$ Hexagonal 01-167-0146	Na Na_2CO_3 Monoclinic 01-164-1148
10	10	80	10	✓								✓	
11	10	70	20	✓								✓	
12	10	60	30	✓								✓	
13	10	50	40	✓								✓	
14	10	40	50	✓								✓	
15	10	30	60	✓								✓	
16	10	20	70	✓								✓	
17	10	10	80	✓								✓	
18	20	70	10	✓								✓	
19	20	60	20	✓								✓	
20	20	50	30	✓								✓	
21	20	40	40	✓								✓	
22	20	30	50	✓								✓	
23	20	20	60	✓								✓	
24	20	10	70									✓	
25	30	60	10		✓	✓						✓	
26	30	50	20		✓	✓						✓	
27	30	40	30		✓	✓						✓	
28	30	30	40		✓							✓	
29	30	20	50		✓							✓	
30	30	10	60									✓	
31	40	50	10		✓	✓				✓			
32	40	40	20		✓	✓				✓		✓	
33	40	30	30		✓	✓				✓		✓	
34	40	20	40										
35	40	10	50										
36	50	40	10				✓			✓			
37	50	30	20				✓			✓			
38	50	20	30							✓			
39	50	10	40							✓			
40	60	30	10				✓		✓	✓			
41	60	20	20				✓		✓	✓			
42	60	10	30				✓		✓	✓			
43	70	20	10					✓	✓	✓	✓	✓	✓
44	70	10	20					✓	✓	✓	✓	✓	✓
45	80	10	10					✓	✓	✓	✓	✓	✓

NOTE 1: L-phase, Low-temperature carnegieite; Nph, Nepheline; Zeo, Zeolite; SAS-1, Sodium aluminum silicate-1; SAS-2, Sodium aluminum silicate-2; S_t, Sodium trisilicate; S_m, Sodium metasilicate; S_p, Sodium pyrosilicate; Qtz, Quartz; Na, Sodium carbonate.

NOTE 2: ✓ indicates that the phase was observed by XRD in mixture after calcining at 850 °C.
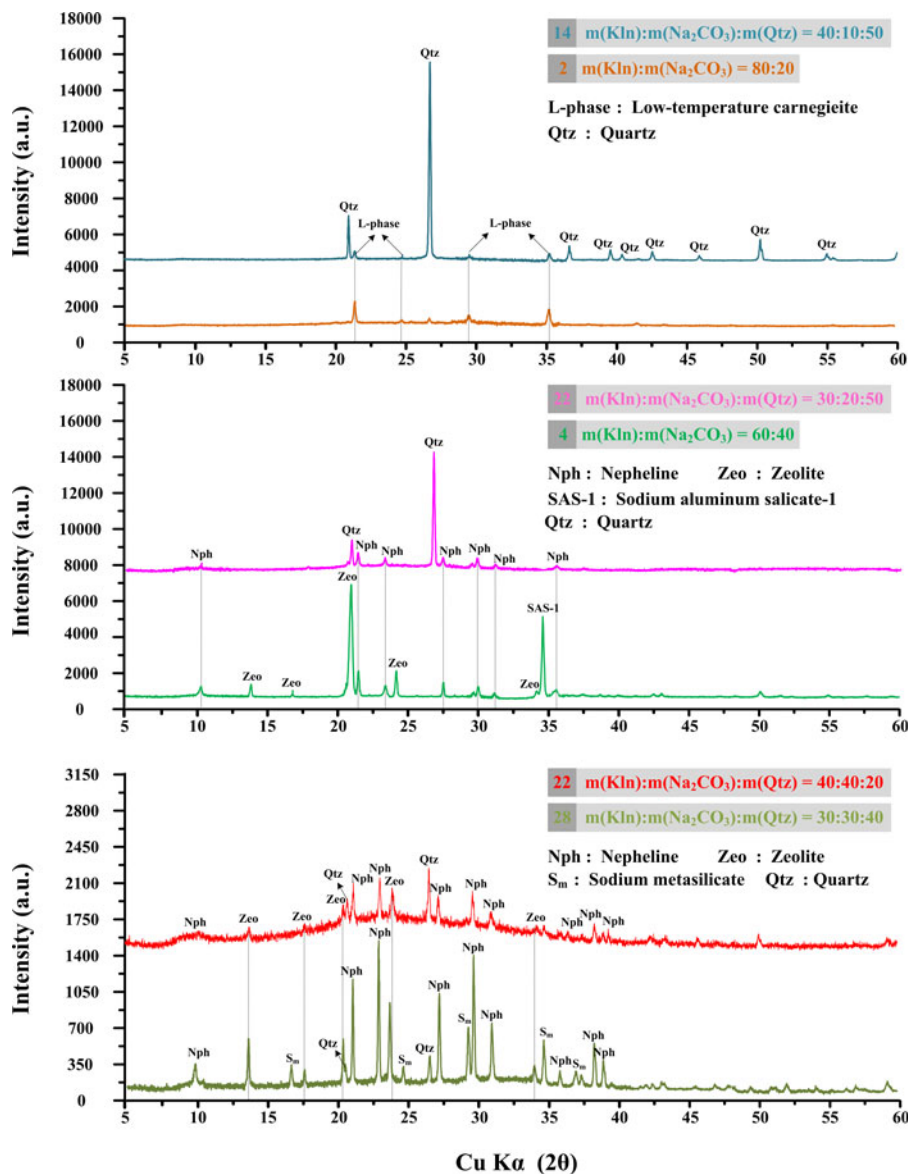
Figure 4. XRD patterns of Kln–Qtz–Na$_2$CO$_3$ quasi-ternary system calcined at 850 °C.

For Kln–Qtz–Na$_2$CO$_3$ system, the formed sodium silicates were derived from the reaction of Qtz and Na$_2$CO$_3$, on the one hand; and from the reaction of Kln and Na$_2$CO$_3$, on the other hand, just as above-mentioned. Generally, it was difficult to limit the reaction of Na$_2$CO$_3$ and Qtz for the Kln–Qtz–Na$_2$CO$_3$ system, since the reaction of Qtz and Na$_2$CO$_3$ could also spontaneously occur at about 850 °C (Gibsont and Ward, 2010). In contrast, it was easy to control the formation of sodium silicates from the reaction of Kln and Na$_2$CO$_3$. As shown in Table II, sodium silicates derived from the reaction of Kln and Na$_2$CO$_3$ were formed when the mass percentage of Na$_2$CO$_3$ was > 40% for the Kln–Na$_2$CO$_3$ system. But for the Kln–Qtz–Na$_2$CO$_3$ reaction system, the formation of these sodium silicates needed more consumption of Na$_2$CO$_3$ due to the effect of Qtz (in Table III). Only when the mass percentage of Na$_2$CO$_3$ was more than 50%, SAS-1 or SAS-2 as well as sodium silicates were detected for the Kln–Qtz–Na$_2$CO$_3$ system calcined at 850 °C. Therefore, in order to control the formation of sodium silicates from the reaction of Kln and

Na$_2$CO$_3$ and further reduce the consumption of Na$_2$CO$_3$, the amount of Na$_2$CO$_3$ added to coal gangue should not exceed 50% of the total mass of Kln, Qtz, and Na$_2$CO$_3$.

Based on this, a reasonable batching area of coal gangue calcined with Na$_2$CO$_3$ at 850 °C is depicted in Figure 6, where the dotted lines represent the mass ratio of Kln to Qtz (Kln/Qtz = 0.28–4.67) in coal gangue and the solid lines represent the reasonable limitation of mass percentage of Na$_2$CO$_3$ (20–50%). Within this limited area, the object activated products of Nph and Zeo could form and the byproducts of sodium silicates might be controlled as much as possible in the calcined products.

V. CONCLUSION

The comparative study of isothermal solid-state reaction systems of Kln–Na$_2$CO$_3$ and Kln–Qtz–Na$_2$CO$_3$ was performed in this work. The main results obtained were as follows:
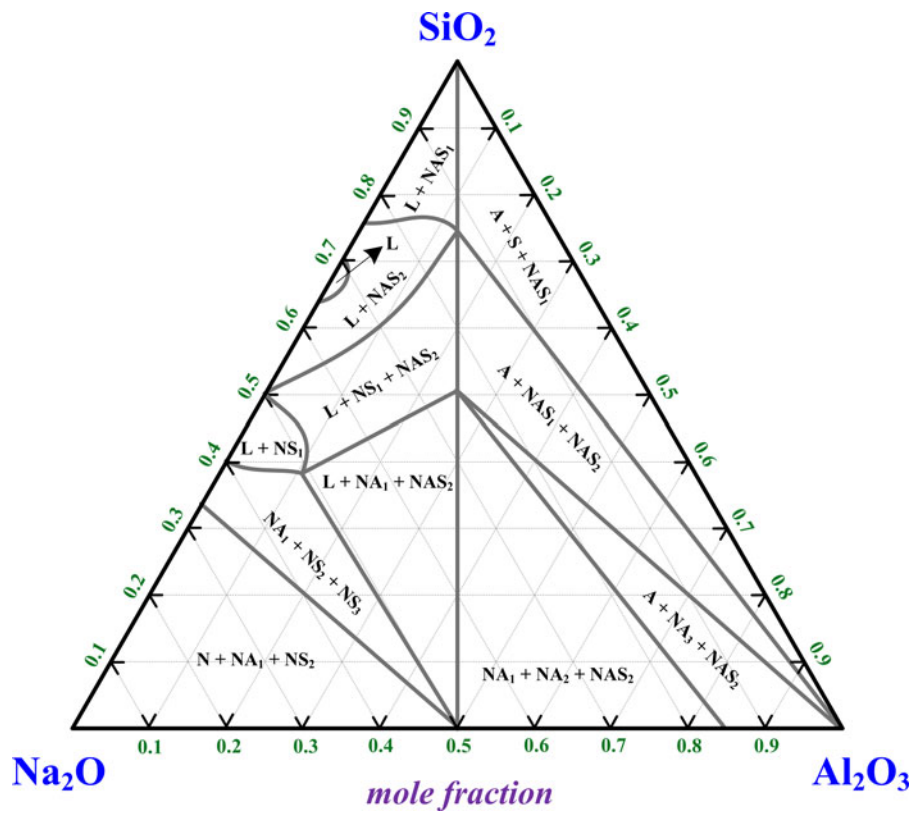
Figure 5. Thermodynamic phase diagram of $Na_2O–Al_2O_3–SiO_2$ system at 850 °C. $N = Na_2O$, $A = Al_2O_3$, $S = SiO_2$; $NA_1 = NaAlO_2$, $NA_2 = Na_2Al_{12}O_{19}$, $NA_3 = NaAl_9O_{14}$; $NS_1 = Na_2SiO_3$, $NS_2 = Na_4SiO_4$, $NS_3 = Na_6Si_2O_7$; $NAS_1 = NaAlSi_3O_8$, $NAS_2 = NaAlSiO_4$.
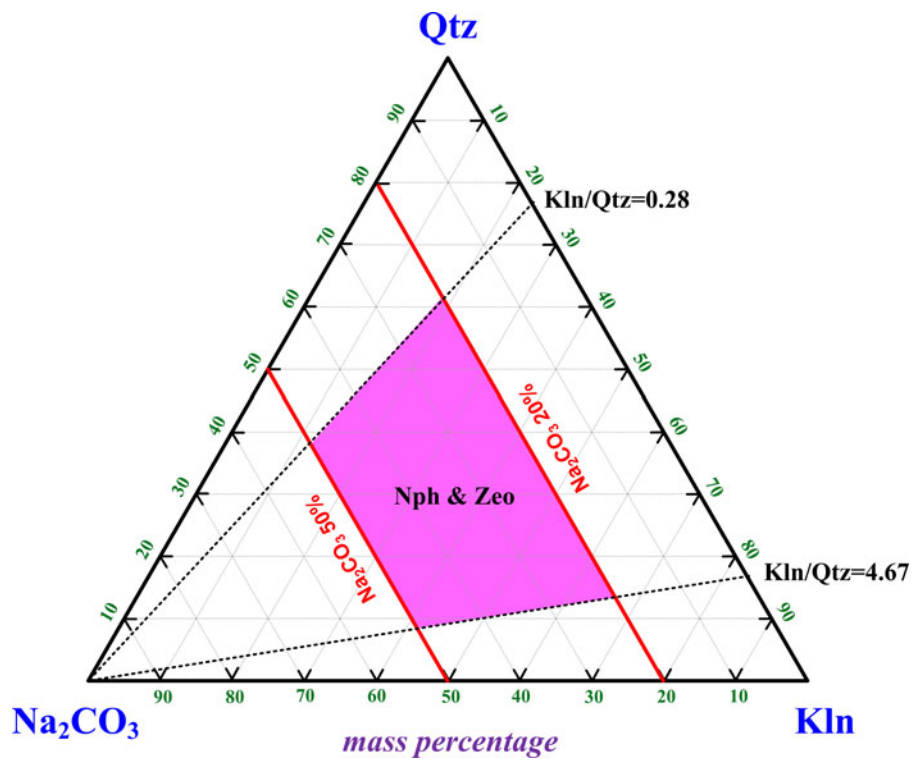

Figure 6. Reasonable batching area (in pink) of coal gangue calcined with Na_2CO_3 at 850 °C.

(1) The phase compositions of Kln–Na_2CO_3 quasi-binary system calcined at 850 °C mainly contain five kinds of sodium aluminum silicates (L-phase, Nph, Zeo, SAS-1, and SAS-2) and three kinds of aluminum-free phases ($Na_2Si_3O_7$, Na_2SiO_3, and $Na_6Si_2O_7$). The mass percentage of Na_2CO_3 in the initial reactant mixtures obviously

had an effect on the phase compositions of the calcined products, determining the Na/Al/Si molar ratio of sodium aluminum silicates.

(2) The phase compositions of Kln–Qtz–Na_2CO_3 quasi-ternary system calcined at 850 °C were similar to that of Kln–Na_2CO_3 quasi-binary system calcined at the same temperature. The mass percentage of Na_2CO_3 in the initial reactant mixtures was still one of the most key factors influencing the phase compositions of the calcined products. However, the existence of Qtz inhibited the formation of these sodium aluminum silicates in the calcined products. The high mass percentage of Qtz was not favorable to the formation of those aluminum-rich and silicon-deficit phases.

(3) The phase compositions of Na_2O–SiO_2–Al_2O_3 system calculated by the FactSage™ software were slightly different from that of Kln–Na_2CO_3 and Kln–Qtz–Na_2CO_3 systems measured in the calcination experiment. The independent sodium aluminates were observed in the calculated results of Na_2O–Al_2O_3–SiO_2 system; while these phases were replaced by the sodium aluminum silicates with high Al/Si ratio in the experimental results of Kln–Na_2CO_3 and Kln–Qtz–Na_2CO_3 systems.

(4) The reasonable batching area of coal gangue calcined with Na_2CO_3 at 850 °C was proposed based on the calculated results of Na_2O–Al_2O_3–SiO_2 system and the experimental results of Kln–Na_2CO_3 and Kln–Qtz–Na_2CO_3 systems, where the addition of Na_2CO_3 should be in the range of 20–50% of the total mass of Kln, Qtz, and Na_2CO_3.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715622000434.

FUNDING

Chao, L., Wan, J., Sun, H., and Li, L. (**2010**). "Investigation on the activation of coal gangue by a new compound method," J. Hazard. Mater. **179**(1–3), 515–520.

Cheng, F., Cui, L., Miller, J. D., and Wang, X. (**2012**). "Aluminum leaching from calcined coal waste using hydrochloric acid solution," Miner. Process. Extr. Metall. Rev. **33**, 391–403.

Gibsont, G. and Ward, R. (**2010**). "Reactions in solid state: reaction between sodium carbonate and quartz," J. Am. Ceram. Soc. **26**, 239–246.

Guo, Y., Li, Y., Cheng, F., Wang, M., and Wang, X. (**2013**). "Role of additives in improved thermal activation of coal fly ash for alumina extraction," Fuel Process. Technol. **110**, 114–121.

Guo, Y., Yan, K., Li, C., Cheng, F., and Lou, H. H. (**2014a**). "Effect of Na_2CO_3 additive on the activation of coal gangue for alumina extraction," Int. J. Miner. Process. **131**, 51–57.

Guo, Y., Zhang, Y., and Cheng, F. (**2014b**). "Industrial development and prospect about comprehensive utilization of coal gangue," J. Chem. Ind. Eng. **65**, 2443–2453 (in Chinese).

Guo, Y., Yan, K., Cui, L., and Cheng, F. (**2016**). "Improved extraction of alumina from coal gangue by surface mechanically grinding modification," Powder Technol. **302**, 33–41.

Hu, F., Wang, W., Yang, X., Hu, Q., Zhao, H., Li, Y., and Li, P. (**2008**). "Ions dissolving properties of activated coal gangue," Coal Conversion **31**, 98–101 (in Chinese).

Jabłońska, B. (**2012**). "Sorption of phenol on rock components occurring in mine drainage water sediments," Int. J. Miner. Process. **104–105**, 71–79.

Ji, H., Fang, M., Huang, Z., Chen, K., Li, W., and Liu, Y. G. (**2014**). "Phase transformation of coal gangue by aluminothermic reduction nitridation: influence of sintering temperature and aluminum content," Appl. Clay Sci. **101**, 94–99.

Kubo, Y., Yamaguchi, G., and Kasahara, K. (**1966**). "Inverted phase relation in formation of nepheline and carnegieite from the system kaolinite-sodium carbonate," Am. Mineral. **51**, 516–521.

Kubo, Y., Yamaguchi, G., and Kasahara, K. (**1967**). "Reaction processes to form nepheline-carnegieite minerals from various starting materials," Mineral. J. **5**(3), 213–223.

Kubo, Y., Yamaguchi, G., and Kasahara, K. (**1968**). "Kinetic and electron optical studies of the reaction process between kaolinite and sodium carbonate," Am. Mineral. **5**(3), 917–928.

Lambotte, G. and Chartrand, P. (**2013**). "Thermodynamic modeling of the (Al_2O_3+Na_2O), (Al_2O_3+Na_2O+SiO_2), and (Al_2O_3+Na_2O+AlF_3+NaF) systems," J. Chem. Thermodyn. **57**, 306–334.

Liu, Q., Jin, H., Zhu, M., Li, H., and Wang, M. (**2014**). "Phases transformation and activity of aluminum and silicon during roasting process of coal gangue," Hydrometallurgy of China **33**, 222–225. (in Chinese).

Lü, Q., Dong, X., Zhu, Z., and Dong, Y. (**2014**). "Environment-oriented low-cost porous mullite ceramic membrane supports fabricated from coal gangue and bauxite," J. Hazard. Mater. **273**, 136.

Schairer, J. F. and Bowen, N. L. (**1956**). "The system Na_2O-Al_2O_3-SiO_2," Am. J. Sci. **254**, 129–195.

Shi, T., Xu, B. W., and Shi, H. S. (**2008**). "The evolution of coal gangue (CG)–calcium hydroxide (CH)–gypsum–H_2O system," Mater. Struct. **41**, 1307–1314.

Tosoni, S., Doll, K., and Ugliengo, P. (**2006**). "Hydrogen bond in layered materials: structural and vibrational properties of kaolinite by a periodic B3LYP approach," ChemInform **37**, 2135–2143.

Vassilev, S. V. and Vassileva, C. G. (**1996**). "Occurrence, abundance and origin of minerals in coals and coal ashes," Fuel Process. Technol. **48**, 85–106.

Xiao, J., Li, F., Zhong, Q., Bao, H., Wang, B., Huang, J., and Zhang, Y. (**2015**). "Separation of aluminum and silica from coal gangue by elevated temperature acid leaching for the preparation of alumina and SiC," Hydrometallurgy **155**, 118–124.

Yan, K., Guo, Y., Wu, X., and Cheng, F. (**2016**). "Effect of organic matter on the Rietveld quantitative analysis of crystalline minerals in coal gangue," Powder Diffr. **31**(3), 185–191.

Yan, K., Guo, Y., Fang, L., Cui, L., Cheng, F., and Li, T. (**2017**). "Decomposition and phase transformation mechanism of kaolinite calcined with sodium carbonate," Appl. Clay Sci. **147**, 90–96.

Yang, M., Guo, Z., Deng, Y., Xing, X., Qiu, K., Long, J., and Li, J. (**2012**). "Preparation of CaO-Al_2O_3-SiO_2 glass ceramics from coal gangue," Int. J. Miner. Process. **102-103**, 112–115.

Yu, L. J., Feng, Y. L., and Yan, W. (**2012**). "The current situation of comprehensive utilization of coal gangue in China," Adv. Mater. Res. **524-527**, 915–918.

Zhang, Y., Xu, L., Seetharaman, S., Liu, L., Wang, X., and Zhang, Z. (**2015**). "Effects of chemistry and mineral on structural evolution and chemical reactivity of coal gangue during calcination: towards efficient utilization," Mater. Struct. **48**, 2779–2793.