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# Micro-scale study of mineral transformation and coverability at single coal char particle surface during high-temperature gasification process

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# ABSTRACT

During the high-temperature coal gasification process, mineral transformation is essential to the formation of residual carbon and ash/slag discharge. The current work investigated the mineral transformation and coverability of the single coal char particle with various ash content during gasification, as well as established the correlation between the ash layer and carbon conversion. Three stages of the gasification process at 1350 °C were defined by the quadratic difference method based on the interaction between the char and the liquid slag, and the two critical points that distinguish the three stages were between 15%–20% and 71%–90% respectively. Further investigation showed that the melting behavior of coal char during gasification was affected by the inhomogeneous distribution of elements. Ca showed a tendency to migrate from the unmolten area to the molten area. The migration behavior was attributed to the eutectic formation between silica-aluminate in the molten area and calcium salts in the unmolten area, leading to a reduction in melting point and gradual melting of minerals in the unmolten area. Eventually, a homogeneous gehlenite phase was formed and covered on the residual char surface. Besides, the relationship between liquid slag coverage and carbon conversion was established, and for SF, YL, and XLT chars, the maximum coverage of liquid product occurs at the conversion of 0.86, 0.78, and 0.66, respectively. This paper provides an in-depth understanding of the slag melting behavior and residual carbon formation in the entrained gasifiers.

### 1. Introduction

With the implementation of China's carbon neutral policy, energy industries using coal as the main resource face great pressure of carbon emission reduction, and thus the clean and highly efficient utilization of coal is an urgent task [1]. The entrained flow gasification technology is key to converting coal to clean energy and reducing carbon emission, while the discharged carbon-rich fine slag will significantly affect the efficiency and waste carbon resources [2]. To further improve the gasification efficiency and reduce the carbon loss as residue in the fine slag, the interaction between the coal ash and gasification is essential.

In the process of coal gasification, the interaction between coal ash and organic matter conversion was found to be highly-related to the formation of carbon-rich fine slag, especially for low-rank coal. According to the survey, China has a vast low-rank coal resource exceeding 500 billion tons, amounting to approximately 11.5% of the worldwide reserves [3]. Low-rank coal has the characteristics of high ash content, low ash melting point, and metal phase content (Ca, K, Na, Fe, et al.), leading to severe challenges in slagging discharge. Such challenges affect the application and promotion of efficient gasification applications in the energy industry [4].

High-temperature coal gasification is a complex process involving multiple physical and chemical phenomena occurring simultaneously. The mineral content of coal is recognized as one of the most important parameters affecting the conversion efficiency, product quality, and equipment safety of coal gasification [5]. During coal gasification, minerals in coal undergo various physical and chemical transformations, including phase transformation, melting, vaporization, and reactions

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with the gasification atmosphere [6,7]. Such changes can alter the mineralogical structure and composition of coal and produce a variety of mineral products, such as aluminosilicates, carbonates, metallic iron, and vitrified slag. Simultaneously, the ash slag melts at high temperature, forming liquid slag that deposit on the walls of the gasifier during the gasification [8]. The mineral transformation and melting behavior of coal ash during gasification have attracted increasing attention [9,10].

The mineral transformation of coal slag includes the chemical reaction between minerals or with the gasification atmosphere, resulting in the generation of new mineral products. The transformation process during gasification is influenced by several factors such as the temperature, pressure, and the gasification atmosphere [2,11]. Shen et al. [12] studied the slag composition in different regions within the wall in the entrained flow gasifier and found that residual carbon and temperature were the dominant influences on mineral variations in different regions, and increased residual carbon content and changing iron valence state increased the mineral types when the slag temperature was below the ash fluid temperature. Liu et al. [6] found that the introduction of water vapor into the gasifier augments the concentration of silicate anions in the slag, thereby enhancing the degree of polymerization of the silicate slag. In addition, compared to CO<sub>2</sub>, water vapor promotes the migration of alkali metals in the slag to the gas phase, consequently altering the mineral phase composition of the coal char surface slag. The melting behavior of coal minerals could produce various products such as vitrified slag, glassy ash, and crystalline ash.

Moreover, coal ash has a significant effect on the physical and chemical properties of char [13,14], while various studies have demonstrated the impact of minerals in catalysts on coal char gasification reactivity [15]. These minerals transform and lose catalytic properties above 1300 °C [16,17]. A plausible explanation is the formation of silica-aluminates at high temperatures [18], but there is no direct evidence to explain this phenomenon. Furthermore, the mineral composition of coal char exhibits a considerable variance under high and lowtemperature environments, and the mineral melting process and transformation mechanism under high temperatures remain unclear. Melting behavior during high temperatures is also an important topic, which has a significant impact on the overall efficiency of the gasification process [19]. Coal ash minerals melt at high temperatures, forming a liquid slag that deposits on the inner walls of the gasifier. The deposits result in severe operational issues, such as gasifier blockages, corrosion of equipment, and fouling of heat exchange surfaces [20,21].

Therefore, the fundamental understanding of the mineral transformation and melting behavior of coal particles during hightemperature gasification is critical for improving gasification efficiency and smooth slag discharge. Several studies have been conducted in this field, focusing on the char slag interactions and the fouling behavior of minerals in coal ash during gasification, and methods to control agglomeration and reflux were proposed, such as mineral additive injection or blending of fuels [21-23]. Techniques like thermodynamic modeling viscosity modeling and/or a combination of techniques were used to predict the slag formation and viscosity with relative accuracy [24]. Although previous research has partially elucidated the melting behavior and mineral transformation after gasification. There remains a paucity of research regarding the evolution and pathway of liquid product formation and mineral transformation throughout the entirety of gasification. Such further research is essential for bolstering the understanding of char-slag interactions and exploring the mechanisms driving mineral transformation.

In this study, mineral transformation and ash melting behavior on the coal char surface of a single particle during gasification were investigated by visualization and surface analytical techniques. In-situ high-temperature hot-stage experiments combined with ImageJ software-assisted image analysis were employed to investigate the charslag interactions of coal char with varying ash contents at different reaction stages. Subsequently, the initial, middle, and last reaction stages of the reaction were reclassified and the critical reaction parameters were defined. The molten/unmolten microstructure of minerals on the particle surface and the elemental distribution of the slag layer during gasification were analyzed by scanning electron microscopy (SEM) combined with energy dispersive spectrometry (EDS), and the influence of the predominant elements on the partial melting behavior was analyzed. The mineral transformation process in the slag layer during gasification was further investigated by combining XRD and in situ Raman. Finally, the relationship between the coverage of surface solid slag during gasification and the conversion rate of the reaction was determined, and the liquid slag layer on the particle surface and char interaction mode in different reaction stages was proposed.

## 2. Materials and methods

### 2.1. Materials

In this study, to investigate the effect of ash content on the inclusions on the surface of a single coal particle during high-temperature gasification, three pyrolytic coal chars with different ash contents were selected as the experimental raw materials, including Shenfu coal char (9.80 wt%), Yili coal char (14.02 wt%), and Xiaolongtan coal char (22.38 wt%), and the samples were abbreviated as SF, YL, and XLT respectively. The ash content significantly affects the reaction and conversion of coal particles during the entrained flow gasification, as a key factor receiving wide attention [1,5,20]. The coal char samples were prepared in a drop tube furnace at 1300 °C under an argon atmosphere, and the feeding rate of raw coal samples was set to 200 g/h. In compliance with the feeding prerequisites of an industrial entrained flow gasifier, coal chars with a particle size of about 100 µm were selected for gasification experiments in this study. The proximate and ultimate analyses of three coal chars were carried out on a 5E-MACIII (Kaiyuan company, China) and a Vario MACRO element analyzer (Elementar, Germany), the results are shown in Table. 1.

The coal ash samples were obtained after combustion in an airambient muffle furnace at 815 °C. The compositions of the three samples were measured by Advant'X Intellipower<sup>TM</sup> 3600 X-ray fluorescence (XRF, Thermo Fisher Scientific, America) and the result is shown in Table 2. The coal ash compositions of YL and XLT are similar, with a relatively high sulfur content in the ash residue. In comparison, SF ash displays notable differences, with a primary structure consisting of silica-aluminates.

The ash fusion temperatures (AFTs) of coal ash under the CO/CO<sub>2</sub> atmosphere were measured by the 5E-AF4000 ash fusion point tester (Kaiyuan, China), and the results are shown in Table 3. YL and XLT coal ash compositions are similar and both have higher ash fusion temperatures while those of SF ash were comparatively lower. Based on the preliminary experiment conducted on the high-temperature hot stage to investigate the melting behavior of coal ash, it was observed that complete melting of coal ash can be achieved at a temperature of 1350 °C. Therefore, the subsequent experimental temperature conditions were chosen to be 1350 °C.

#### 2.2. Methods

In this study, the TS1500 in-situ high-temperature hot stage (Linkam, U.K.) coupled with a DM4500P light-emitting diode microscope (Leica, Germany) was applied to investigate the gasification process of different char particles, and this method had been widely used in the in-situ study of high-temperature gas–solid reactions [25,26]. The char samples were spread on the sapphire slip (Al<sub>2</sub>O<sub>3</sub>, 99% purity) and then placed in the ceramic crucible (7 mm in diameter, 3 mm in height). Before gasification, the ceramic crucible and samples in the chamber were first heated to 105 °C at the heating rate of 50 °C/min to preheat the apparatus and remove the moisture. Then, the temperature rose to 1350 °C at the heating rate of 100 °C/min in Ar (100 mL/min), and the samples were held for 3 min at the temperature of 1350 °C to stabilize the particle

#### Table 1

Proximate and ultimate analyses of samples used in this study.

Proximate analysis (ad, wt. %)					Ultimate analysis (ad, wt. %)				
Components	М	V	FC	А	С	Н	S	Ν	0*
SF	3.32	5.42	81.46	9.80	83.35	1.02	0.30	0.98	1.22
YL	1.52	3.29	81.17	14.02	81.27	0.39	1.07	1.31	0.41
XLT	3.47	6.23	67.92	22.38	67.32	0.64	2.94	1.31	2.01

<sup>\*</sup> The oxygen content was obtained by difference.

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Chemical compositions (wt.%) of coal ash.

Ash	Component	Component content(wt.%)							
	SiO <sub>2</sub>	CaO	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	MgO	Na <sub>2</sub> O	$SO_3$
SF	35.02	29.07	17.72	11.98	0.55	0.56	0.98	3.22	0.90
YL	21.86	24.84	11.14	16.73	0.33	0.43	5.04	0.77	18.61
XLT	22.90	22.62	14.66	14.03	0.59	0.56	4.86	0.45	18.83

#### Table 3

Ash fusion temperature (AFTs) of different coal chars.

AFTs*	DT (°C)	ST (°C)	HT (°C)	FT (°C)
SF	1168	1178	1187	1224
YL	1303	1322	1324	1334
XLT	1305	1337	1345	1349

<sup>\*</sup> DT: deformation temperatures; ST: soften temperatures; HT: hemispherical temperature; FT: flow temperature.

temperature. Then,  $CO_2$  (10 mL/min) was injected into the chamber and reacted with char particles. Meanwhile, a camera on the microscope was turned on to record the whole reaction process. To obtain char particles with different conversions, the inlet time of  $CO_2$  was strictly controlled, and a large volume of Ar was injected after gasification to cool and terminate the reaction rapidly. After gasification, SEM-EDS (Hitachi, Japan) was used to analyze for element distribution and structure of the samples. In addition, mineral compositions of coal ash were measured by a PANalytical X' pert Powder X-ray powder diffractometer (XRD) with Cu K $\alpha$  radiation. Crystalline minerals were further analyzed by Jade 6.5 software based on the XRD patterns of the samples. Raman spectroscopy (ThermoFisher Scientific, America) was used to analyze the structure of the cooled particle in the different reaction areas (see Fig. 1).

ImageJ software was used to measure the cross-sectional area of char particles during gasification [27]. The char particle can be assumed to be

a density homogeneous particle and the conversion can be obtained as a shrinking particle. Therefore, the relationship between the particle diameter ( $d_t$ ) and cross-sectional area ( $A_{t,i}$ ) at time *t* was:

$$d_t = 2\sqrt{\frac{A_t}{\pi}} \tag{3}$$

For a spherical particle with uniform density, the carbon conversion can be calculated as:

$$x_{i} = \frac{m_{0} - m_{t}}{m_{0} - m_{1}} = \frac{\rho V_{0} - \rho V_{t}}{\rho V_{0} - \rho V_{1}} = \left(\frac{A_{0,i} - A_{t,i}}{A_{0,i} - A_{1,i}}\right)^{3/2}$$
(4)

$$\overline{x} = \sum_{i=1}^{n} \frac{x_i}{n} \tag{5}$$

where  $A_{0,i}$  is the initial particle cross-sectional area,  $\mu m^2$ ,  $A_{1,i}$  is the particle cross-sectional area at the end of the reaction,  $\mu m^2$ .

#### 3. Results and discussion

#### 3.1. In-situ gasification process

The in-situ gasification reaction processes of SF, YL, and XLT coal chars at 1350  $^{\circ}$ C are shown in Fig. 2. The coal char particles with varying ash contents underwent rapid shrinkage after the reaction initiated and



Fig. 1. The schematic diagram of the visual experimental platform.



Fig. 2. In-situ gasification processes of char particles with various ash content.

shrunk to a minimum projection area in a relatively short period. During the gasification process, the visual appearance of the coal char projection was black while the molten slag appeared translucent and was gradually exposed around the residual carbon in the middle and late stages of the reaction. Based on the ash content and melting behavior, particles displayed varying degrees of shrinkage through the reaction. The particle size of the translucent slag after the reaction corresponded to the ash content. Additionally, the overall reactivity of different samples also differed, with the entire gasification average reaction times of 14.0 s, 11.2 s, and 8.7 s for SF, YL, and XLT coal chars, respectively. The reaction time for high ash coal char (XLT) was more than 1/3 shorter than that of low ash coal char (SF), providing evidence of the catalytic effect of ash on coal gasification [28].

The black projection area variation of the particles of different coal samples is shown in Fig. 3(a), and the carbon conversion curves calculated by Eq. (4) are shown in Fig. 3(b). The liquid slag layer generated after the gasification of char particles still exhibited a certain cross-sectional area due to the influence of ash content, but it would not change with reaction time after the reaction. As shown in Fig. 3(b), the overall conversion rate of coal char particles displayed a three-stage reaction trend of "slow-fast-slow" during the reaction process. In the initial stage, the reaction rate was slow but increased rapidly, the middle stage is characterized by a rapid reaction rate, while the late stage is slow and persistent. Under 1350 °C conditions, significant differences in

reaction rates were observed among different coal chars, particularly in the middle stage, which may be attributed to differences in char structure and ash content.

Fig. 3 illustrates the overall trend of the gasification processes of SF, YL, and XLT coal char. However, a clear distinction between the initial middle and late stages requires careful consideration. Studies showed that the gasification reaction under coal char at high temperatures (>1300 °C) is mainly affected by gas–solid contact and bed diffusion resistance [29,30]. For a single-particle gasification reaction, the influence of diffusion on the reaction is mainly reflected in two aspects: particle pore structure and slag melt adhesion. The pore exposure and expansion in the initial stage of the reaction promote gas–solid contact and facilitate gasification. However, in the middle and later stages, molten slag covers the residue carbon surface, hindering the reaction. The combined effect of these two interactions affects the gasification rate, and this effect requires further detailed discussion for a single-particle gasification process.

The conversion rate curves were subjected to primary and secondary differencing, and the gasification reaction rate ( $r_a$ ) and reaction rate change curves ( $dr_a/dt$ ) were obtained as shown in Fig. 4(a). The gasification reactivity of XLT coal char is higher than YL and SF coal char. Specifically, the reaction rate of three types of coal char exhibited an initial increase followed by a subsequent decrease, and the maximum reaction rates of XLT, YL, and SF char decreased in sequence. During the



Fig. 3. Evolution of cross-sectional area (a) and conversion x (b) of different coal char at 1350 °C.



Fig. 4. Plots of gasification rate and reaction rate variation (a) reaction stages (b) and critical parameters versus relative time (c).

initial and middle stages, the reaction rate of XLT coal char was higher than others. However, in the later stage, the reaction rate experienced a rapid decline and was lower in both YL and SF coal chars due to the liquid cover on the char particle. Due to the high volatile content of XLT lignite, the pyrolytic coal char demonstrates extensive pore development and exhibits high carbon activity, and the high ash content means a heightened amount of catalytic metal elements [4,10,28]. Hence, the reaction rate of XLT coal char was faster than others in the early stage. With the progress of the reaction, due to the high ash content and the slag coating caused by ash melting in Fig. 5, the slag cover leads to a decrease in the reaction rate. The reaction rates of the three types of coal char showed an increasing–decreasing trend, The second-order differential provides greater detail than the first-order differential, and it demonstrates the effect of carbon structure and slag adhesion on the reaction rate.

Based on the second-order differential results, the whole reaction can be divided into three parts, namely, the initial, the middle, and late stages, which correspond to the reaction trend of "slow-fast-slow" in Fig. 4(b), respectively. In the initial stage, the reaction rate gradually increased while the gasification rate variation also increased, resulting



Fig. 5. Particle morphology evolution during XLT coal char gasification.

in a "faster and faster" trend. In the middle stage, the reaction rate increased and then decreased. Whereas, the variation of reaction rate kept decreasing, indicative of the onset of "resistance" that hinders the reaction. In the late stage, the reaction rate decreased and leveled off, with the reaction rate decrease continuing to lessen. The result proved that the influence of "diffusion resistance" on the reaction had reached the maximum level.

The second-order curve exhibits two extreme points, characterized by the maximum values of reaction rate increment and decrement, respectively. The former point can be considered as the extreme point of the effect of the pore structure on the reaction rate, while the latter represents the extreme point of the effect of the liquid slag layer wrapping on the reaction rate. The corresponding critical reaction times were named  $t_{e1}$  and  $t_{e2}$  and the critical conversion rates were named  $x_{e1}$  and  $x_{e2}$ , as shown in Fig. 4(c). The ratio of the first critical reaction time to total reaction time  $(t_{e1}/t_{total})$  ranged from 0.24 to 0.33 for the three kinds of char gasification, and  $t_{e2}/t_{total}$  ranged from 0.46 to 0.58. Further, about 50% of the reaction time was consumed during the reaction of residual 20% carbon in the late stage, which seriously hindered the reaction process. The influence of ash content was further analyzed. Comparing the results of different chars, the ash content was negatively correlated with the critical conversion rate  $x_{e2}$ , which was 71.38% for XLT coal char with 22.38% ash content, 79.59% for YL coal char with14.02% ash content, and 90.24% for SF coal char with 8.80% ash content. High ash content was more detrimental to the late stage of gasification. In entrained gasifiers, the presence of liquid slag is an important cause of incomplete coal-char gasification and residual carbon formation.

#### 3.2. Slag formation and melting process

The full (partial) enlarged view of the XLT samples after in-situ gasification at various conversions is shown in Fig. 5. The coal char particles were controlled to attain different conversion rates by manipulating the inlet time of the reaction gas along with measures of rapid cooling after the reaction, The projected area of the particles before and after the reaction was obtained through ImageJ under the specified condition. The conversion of a single particle was determined based on Eq. (4), and the average conversion is further obtained as the conversion of each particle in this group of experiments.

It can be observed from Fig. 5(a) to Fig. 5(b) that at the initial stage of the reaction, the coal char surface developed clear honeycomb pores, and exposed ash partially molten to form spherical particles of varying

size adhering to the surface of the coal char. The liquid spheres formed by a small amount of ash were distributed independently and randomly and did not obscure the pores on the coal char surface, implying a minor effect on the reaction. As the reaction proceeded to about 34% as shown in Fig. 5(c), the coal char surface was severely altered, and the pores gradually expanded and assumed the form of gullies. The ash shell structure was revealed, with part of the coal ash melting and aggregating on the coal char surface, forming liquid slag of various shapes. However, most of the ash shell structure was still maintained. When the reaction proceeded to 54%, the particles shrank visibly, and half of the ash layer structure got destabilized and molten to cover the char surface, forming a smooth glassy configuration. At the late stage of the reaction (Fig. 5 (e)), the previously maintained ash shell structure had collapsed entirely, and the liquid slag was included on the surface of the residual carbon. While the residual carbon continued to react, generating pores on the surface of the slag. There was still a small amount of high melting point minerals adhering to the liquid slag layer. Finally, at the end of the reaction (Fig. 5(f)), the ash layer including high melting point minerals was entirely melted and was laid flat on the sapphire.

YL and SF coal char exhibited a similar reaction trend to that of XLT coal char, and the results are shown in Fig. 6. The size and amount of liquid spherical particles formed on the coal char surface corresponded to the ash content during the initial reaction stage. It was also observed that YL coal presented more surface cracks and pores in the initial stage, while dense micropores were presented on the surface of SF coal char. The emergence of cracks proved an increase in the gasification rate. As indicated in Fig. 4(b), it took less time for YL coal char to attain the same critical conversion rate ( $x_{e1}$ ). Indeed, the effect of coal char structure was a vital factor contributing to the differences in reactivity in the initial stage. As the reaction progressed, the coal char continued to converge and the liquid slag wrapped around the residual carbon to form liquid spheres, and macropores were generated on the slag surface, which is related to the continued gasification of residual carbon.

The above study in Fig. 4 divided the whole reaction process into three stages, and the effect of the liquid residue layer on the gasification process can be further speculated by combining the gasification morphology results of the three coal chars. In the initial stage, the reaction rate increased rapidly, and it was attributed to the expansion of the char pore structure, which increased the contact area of the gas-solid reaction. In the middle stage, "resistance" began to hinder the reaction. The primary source of the resistance was the encapsulation of residual carbon by liquid slag, which became increasingly apparent with the reaction. In the late stage of the reaction, the influence of "diffusion



Fig. 6. Particle morphology evolution during YL and SF char gasification.

resistance" on the reaction had reached the maximum level, presumably because the residual carbon was completely wrapped by the molten slag, and the reaction was carried out only through a few remaining pores at the end of the reaction.

#### 3.3. Element distribution

Fig. 7 shows the elemental distribution on the surface of coal char particles during the gasification reaction at 1350 °C. The results showed that the elemental composition of the coal char surface had varied significantly at different stages of the reaction. The surface of the raw char exhibited a subtle aggregation of Si elements and sporadic Fe distribution, potentially linked to iron oxide in the ash. The remaining elements, however, displayed a uniform distribution. For the raw, coal char has low ash content on the particle surface, and the brightness of the elements was low except for carbon and oxygen elements.

In the initial and middle stages (Fig. 7(b)), ash was exposed on the char surface, and different mineral compositions led to distinct melting behaviors in diverse regions of the ash layer. The molten area and surrounding unmolten area exhibited clear elemental differences, with K, Al, Si, and O enriched in the molten area while Ca is enriched in the unmolten area. Fe existed as random iron oxide nanoparticle distributions among the coal char particles as shown in Fig. 7(a), with no distinguishable hematite particles observed in Fig. 7(b). In the late stage of the reaction (Fig. 7(c)), most of the ash was molten and wrapped in the residual carbon, while a small proportion of high melting compounds still adhered to the slag surface. EDS results show that there were obvious differences in elemental composition between the molten and unmolten area, while K, Si, and Al distributed in the molten area, while the non-molten area was still dominated by Ca and Fe. Meanwhile, further observation revealed that during the formation of the liquid

product, the elements showed a migration state, Ca showed the trend of migration from the unmolten area to the molten area, and it was presumed that the silica-aluminate in the melting area formed low melting point eutectic with the calcium salt in the unmolten area, which lowered the melting point and the minerals in the unmolten area with high melting point melt gradually. At the end of the reaction, the slag completely melted to form a smooth surface with a uniform distribution of surface elements, forming a homogeneous mineral phase. It was noteworthy that sulfur elements had a low content on the char surfaces during the reaction process. Most of the sulfur element had been released before the reaction began [31,32].



**Fig. 8.** Relative content of elements in the molten (A<sub>1</sub>) and unmolten regions (A<sub>2</sub>) of different coal ash.

C	0	Al	С	0	Al
10µm	<u>10µт</u>	10µm	<u>10µт</u>	<u>10µт</u>	10µm
Si	(a)	S	Si	(b)	S
<u>10μm</u>	x≈0%	10μm	10µm	slag $\chi \approx 34\%$	10µm
K	Ca	Fe	K	Ca	Fe
<u>10μm</u>	10µm	<u>10μm</u>	<u>10µт</u>	<u>10µт</u>	<u>10μm</u>
С	0	Al	С	0	Al
<u>20μm</u>	<u>20µm</u>	20µm	10µm	<u>10µт</u>	10µm
Si	(c) <b>7</b>	S	Si	(d)	S
<u>20μm</u>	x≈83%	20µm	10µm	x>99%	10µm
K	Ca	Fe	K	Са	Fe
20µm	20um	20um	10µm	20um	10um

Fig. 7. Element transformation process during gasification at 1350 °C.

Fig. 8 shows the average elemental content of the three coals in the partially molten area ( $A_1$ ) and the unmolten area ( $A_2$ ) in the middle of the reaction. The mineral composition varies greatly depending on the coal type. However, in general, K, Si, and Al form minerals with low melting points and are the first to form the molten area during the reaction. While minerals formed by calcium salts and hematite have a higher melting point and form an unmolten area. The difference in mineral composition on the surface of coal ash led to differences in the fusibility of the ash layer on the particle surface during gasification.

#### 3.4. Mineral evolution

Fig. 9 displays the results of XRD analysis of the primary crystalline structures in ash samples to obtain additional mineral composition information. The ash samples in Fig. 9(a) to 9(c) were obtained from raw coal ash, coal ash after gasification at 1000 °C, and molten coal ash after gasification at 1350 °C, respectively. Raw coal ash had a complex mineral composition. Both YL and XLT coal ash contain high elemental sulfur and are similar in composition, the crystalline phase is dominated by anhydrite. While the ash contained a small amount of hematite lllite and quartz, which were the main forms of elements such as iron aluminum potassium silicon in the original ash. SF coal ash had high silica-aluminum components and little sulfur content, the main mineral composition in the coal ash slag was diopside and anorthite. The crystal structure composition observed in the ash balls, obtained post gasification at 1000 °C, was consistent with that of the raw coal ash, signifying the absence of transformation of the crystal structure of the unmolten coal ash. The differences in peak intensities and marginally varying mineral contents exhibited by gasification coal ash samples have been associated with the non-uniform distribution of mineral fractions present in the coal ash.

After gasification at 1350 °C, the coal ash molten and the mineral

composition of the three residues slag were similar. The previously complex and uneven mineral composition of the coal ash transformed into a uniform gehlenite structure. Regarding SF and XLT coal ash, calcium sulfate decomposed and volatilized during the high-temperature gasification process[31], and sulfate was converted to silicon aluminate. The EDS results in Fig. 7 and Fig. 8 also demonstrated the transformation of this process.

The micro-Raman results show the structural units and composition of anions in the silica-aluminate melt, while the qualitative analysis of crystal composition and content in the minerals relies on the XRD results. Simultaneously, the anionic groups identified in the XRD results exhibit concurrence with the micro-Raman analysis, substantiating the universality of the micro-Raman results. This consistency dismisses the possibility of a fortuitous occurrence stemming from the uneven distribution of elements within the minerals in the coal char particle. By integrating the macroscopic changes in ash composition before and after the gasification reaction obtained through XRD analysis, reasonable speculation concerning the melt phase transition and mineral transformation within the molten and non-molten zones during the gasification process was carried out based on the micro-Raman results of the different reaction stages.

Micro-Raman spectra of coal slag surface of XLT coal with different gasification degrees are shown in Fig. 10. The attribution of Raman spectral bands was summarized according to the relevant literature and the vibrational modes of different structures, and the results are shown in Table 4. The minerals in the initial coal ash sample mainly include calcium sulfate, quartz, potassium feldspar, and hematite, which was consistent with the XRD results in Fig. 9. The vibrational peaks at 1000 cm<sup>-1</sup>, and 612 cm<sup>-1</sup> indicated the presence of anhydrite in XIL coal ash, where the strong and sharp peak at 1000 cm<sup>-1</sup> is associated with the stretching vibration of the sulfate group and the vibrational peak at 612 cm<sup>-1</sup> is attributed to the bending vibration of the sulfate. In addition, the



Fig. 9. XRD results of three kinds of ash samples after gasification at different temperatures: (a) SF ash, (b) YL ash, and (c) XLT ash. 1-Diopside, 2-Anorthite, 3-Anhydrite, 4-Hematite, 5-Quartz, 6-Gehlenite, 7-Lilite.



Fig. 10. Mineral transformation process during gasification at different stages: (a) the raw ash, (b) initial stage, (c) middle stage, and (d) after gasification.

 Table 4

 The correspondence of Raman shift and mineral composition used in this study [36–38].

Wavenumber (cm $^{-1}$ )
617, 1011, 123, 1316
243, 630, 658
1113, 400
477, 606, 584
723, 948
334
610, 648, 714, 897

weak peak at 658 cm<sup>-1</sup> is associated with the bending vibration of Fe-O in hematite, proving that a small amount of iron oxide is still present in the coal ash. The vibrational peaks observed at  $123 \text{ cm}^{-1}$ ,  $400 \text{ cm}^{-1}$ , and  $1113 \text{ cm}^{-1}$  suggest the presence of potassium feldspar in the coal ash residue, which is also the primary form in which potassium elements reside in coal ash. The strong band at  $460 \text{ cm}^{-1}$  arising from symmetric Si-O stretching vibration is related to quartz.

In the initial stage of the reaction, the Raman spectra of the molten area and the unmolten area are shown in Fig. 10(b). The composition of coal ash is a complex mixture of various inorganic compounds, and each vibrational peak between specific valence bonds may be slightly shifted due to the impact of neighboring atoms [33–35]. In the molten area, feldspar diopside, and amorphous SiO<sub>2</sub> were the primary mineral, as evidenced by the vibration peak identified at 400 cm<sup>-1</sup>, 334 cm<sup>-1</sup>, and 584 cm<sup>-1</sup>. Thus, the molten area had a higher elemental silica-alumina content. The minerals have a lower melting point and melt rapidly when exposed to the surface of coal char to form a molten area during gasification. While no anhydrite was found, indicating that its decomposition and silica-aluminate formation had already occurred in the initial stage. Conversely, the unmolten area mainly contained high melting

points ash components, such as hematite and sillimanite, and the unmolten area had a higher content of Ca and Fe as shown in Fig. 8. At the initial stage, these component particles were difficult to form low-temperature eutectics and therefore difficult to melt.

In the middle and late stages of gasification (Fig. 10(c)), the molten area covered most of the residual carbon surface and formed an encapsulated liquid phase. Despite this, a small part of the high melting point compounds still agglomerated on the surface of coal char as shown in Fig. 7(c). Vibrational peaks attributed to gehlenite (714  $\text{cm}^{-1}$ ) and diopside (334 cm<sup>-1</sup>) were observed in the molten area, where the minerals in the liquid slag underwent a transformation and the complex mineral composition gradually homogenized. In the unmolten area, sillimanite and hematite predominated. At the end of the reaction, the liquid phase products completely melt to form liquid slag, and the Raman results are shown in Fig. 10(d). The slag layers at 897 cm<sup>-1</sup>, 712 cm<sup>-1</sup>, etc. proved that only gehlenite existed in the liquid slag after gasification. Therefore, the mineral distribution in the molten area was uniform as shown in Fig. 7(d). The unmolten calcium salts and hematite gradually melted during the reaction stage, presumably due to the low melting point of the molten ash wrapping the unmolten calcium salts and hematite to form eutectic, which was also confirmed by the migration trend of Ca presented in Fig. 7(c). The formation process of eutectic lowered the ash melting point of the material in the unmolten area and affected the melting behavior of the ash particles.

The XRD results presented in Fig. 9 provide a comprehensive analysis of the coal ash composition under varying gasification conditions. The appearance of Gehlenite as a new mineral phase in the XRD data corroborates the findings regarding the migration and combination of surface elements, leading to the formation of low-melting-point compounds. This also suggests that after the gasification reaction, the entire ash area has undergone melting and combined to form a compound with a low melting point, because only the Gehlenite phase is present in the slag after gasification. Concurrently, the micro-Raman results

demonstrate the mineral transformation process within the micro-zones during the gasification process. Notably, upon complete melting, the findings from both techniques align, validating the reliability of the micro-Raman results. Consequently, the relationship between micro-Raman and XRD results is from point to area, complement each other and provide mutual support.

#### 3.5. Effect of molten slag on gasification

The results of EDS provide the phase data and the area share [39,40]. Although the composition of individual mineral phases on the char surface cannot be determined precisely, slag and carbon can be clearly distinguished, as the EDS result provided the major elements in each phase, and it was shown in Fig. 11(a). Accordingly, we can further approximately calculate the relationship between liquid product coverage ( $S_x$ ) and coal char conversion (x) in the gasification process based on Eq. (6).

$$S_x = \left(1 - \frac{A_{C,x}}{A_{total,x}}\right) \left/ \left(1 - \frac{A_{C,0}}{A_{total,0}}\right)$$
(6)

Comparing the results of the three kinds of coal char, the coverage rate of the liquid slag to the ash layer increased rapidly with increasing conversion in the middle of the reaction. For the same conversion of different coal char, liquid product coverage increased with increasing ash content. For the three types of coal char with varying ash contents, the surface coverage of liquid products on the coal char was less than 20% at the first critical conversion point ( $x_{e1}$ ), and a gradual influence on the reaction rate was observed due to the formation of the liquid ash layer. XLT, YL, and SF reached a liquid product coverage of 100% at conversion rates of about 66%, 78%, and 86%, respectively, a trend consistent with the critical conversion point  $x_{e2}$ . The results indicated a rise in residual carbon content with the increase in ash content.

The relationship between coal char and the liquid slag layer in different reaction stages is shown in Fig. 12. At the initial stage of

reaction ( $x < x_{e1}$ ), the slag on the surface of coal char was sporadically distributed and melted to form a liquid globule, and the pores of coal char were obviously increased. As the reaction progressed, the content of slag on the surface increased, and the molten slag aggregated and adhered, giving rise to an increment in ash wrapping on the coal char surface. This agglomeration increased the diffusion resistance of the coal char gasification reaction. At this stage, part of the ash with a high melting point remained exposed to the coal ash surface. As shown in Figs. 3 and 4, the gasification reactivity of XLT coal char is higher than YL and SF coal char. Specifically, the reaction rate of three types of coal char exhibited an initial increase followed by a subsequent decrease. During the initial and middle stages, the reaction rate of XLT coal char was higher than other two coal chars. However, in the later stage, the reaction rate experienced a rapid decline and was lower in both YL and SF coal chars due to the liquid cover on the char particle. Due to the high volatile content of XLT coal, pores of pyrolytic coal char are well developed, and the reaction rate was faster than other two coal chars in the early stage. With the progress of the reaction, due to the high ash content and the slag coating caused by ash melting in Fig. 5, the slag cover leads to a decrease in the reaction rate.

With the gasification of carbon on the surface, the thickness of the slag layer gradually increased. In the late stage, depending on the difference in ash content of various coal types, the residual carbon particles were completely included between 66% and 86% of the reaction conversion, which seriously hindered the diffusion of the gasifier to unreacted nuclei in the particles and led to the decrease of carbon conversion.

#### 4. Conclusion

This study investigated the mineral transformation and melting behavior for coverability on the single particle coal char with various ash content during gasification, as well as the correlation between the ash layer and conversion. According to the research results of coal char



Fig. 11. (a) Phase distribution and relative content of XLT raw coal char, and (b) the relationship between liquid product coverage (S<sub>x</sub>) and coal char conversion (x).



Fig. 12. Schematic diagram of the relationship between coal char and liquid slag layer in different reaction stages.

with different ash contents, three stages of the gasification process at 1350 °C were redivided. While two critical reaction points that were primarily controlled by the pore structure and the liquid slag layer were defined. Further study results demonstrated that the melting behavior of coal char during gasification was influenced by the inhomogeneous distribution of elements. K and Si were enriched in the molten area, while the non-melting area was enriched in Ca and Fe, and had a higher melting point. As the reaction proceeded, the liquid products in the molten area on the char surface gradually wrapped around the unmolten area, and Ca showed a tendency to migrate from the unmolten area to the molten area. The migration behavior was attributed to the eutectic formation between silica-aluminate in the molten area and calcium salts in the unmolten area, leading to a reduction in melting point and gradual melting of minerals in the unmolten area. A homogeneous gehlenite phase was formed and covered on the residual char surface. Eventually, a relationship between liquid slag coverage and carbon conversion was established dependent on ash content and fusion, and for SF, YL, and XLT chars, the maximum coverage of liquid product occurs at the conversion of 0.86, 0.78, and 0.66, respectively.

#### CRediT authorship contribution statement

Haigang Zhang: . Zhongjie Shen: Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. Qinfeng Liang: Writing – review & editing, Visualization, Validation, Supervision, Resources. Jianliang Xu: Writing – review & editing, Visualization, Validation, Supervision, Resources. Xiaolei Guo: Writing – review & editing, Visualization, Supervision, Resources. Zhenghua Dai: Writing – review & editing, Supervision. Haifeng Liu: Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, 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.

# Data availability

The authors are unable or have chosen not to specify which data has been used.

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