

Research Article

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Ash melting behavior and mechanism of high-calcium bituminous coal in the process of blast furnace pulverized coal injection

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Abstract: High-calcium bituminous coal has the advantages on combustibility, but its ash melting point is low, and it is easy to slag in blast furnace injection process. In order to explore the ash melting slag formation mechanism of high-calcium bituminous coal, the mineral evolution of ash in the combustion process of high-calcium bituminous coal and the influence of ash components on the liquid formation in the melting process were studied. The results showed that the melting behavior of ash gradually occurs with the change in the morphology, and the main mineral transformation is carried out around different deposition forms of Ca and Si. The liquid phase formation of ash at high temperature is the essential reason of its melting behavior. The higher the content of CaO, the higher the starting temperature of the liquid phase formation. The higher the content of SiO₂, the lower the starting temperature of the liquid phase formation, and the more the liquid phases generated at a given temperature. Increasing the content of Al₂O₃ can expand the temperature range of reducing the formation of ash liquid phase to 1,473–1,673 K. When the temperature is above 1,573 K, Fe₂O₃ can promote ash liquid phase formation.

Keywords: combustion, coal ash, fusion characteristics, mineral conversion, liquid phase formation

1 Introduction

Fossil energy is the most important energy consumed in the world. With the continuous exploitation by human beings and the large-scale use of fossil energy, the depletion of fossil energy is inevitable, so the development and utilization of low rank coal is very important. China's energy consumption is still dominated by coal. As a pillar industry in China, the iron and steel industry is highly dependent on coal resources [1,2] and coal is an indispensable major energy in the production process of iron and steel enterprises. By studying the feasibility of high-calcium bituminous coal used in blast furnace injection and the influence of pulverized coal injection on blast furnace smelting, the theoretical basis and technical support for the application of high-calcium bituminous coal in blast furnace injection are provided. Based on the combustion characteristics of pulverized coal in the blast furnace tuyere area, many blast furnace injection coal blending technologies are designed [3]. Reasonable utilization of the coal blending technology can improve the stability of pulverized coal combustion in the blast furnace tuyere area, reduce pollutant emissions, and reduce or eliminate slagging in furnace [4]. At the same time, blast furnace ironmaking consumes a large amount of coal resources, and reducing coal consumption is the key to energy conservation and emission reduction [5,6]. Pulverized coal injection in blast furnace is the central link in the structural optimization of ironmaking system, and it is also an important means for iron and steel enterprises to achieve the sustainable development of cost reduction and efficiency increase. It can be used to replace coke as a part of the reducing agent in the reduction reaction of blast furnace [7]. The development of blast furnace coal injection technology and the continuous maturity of pulverized coal preparation and transportation technology have also expanded the source of pulverized coal, and its application as a fuel in metallurgical enterprises has become more and more extensive [8–11]. The ash fusion

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characteristics of pulverized coal injected into the blast furnace have an important influence on the combustion of coal and the ash morphology change in coal during gasification and liquefaction, and are also important parameters to measure the quality of coal [12–15]. Therefore, it is of great significance to study the melting characteristics of coal ash from the perspective of coal ash composition and its minerals for expanding the application range of coal and the mixing of coal injection with low ash melting point [16–21]. In the process of blast furnace smelting, pulverized coal enters the blast furnace through the spray gun and participates in a series of reactions in the furnace. Therefore, problems such as slagging, gun plugging, and corrosion may be caused during the injection process [22–26]. The occurrence of these problems is closely related to the melting characteristic temperature of coal ash. The occurrence of these problems can be effectively improved by regulating the melting characteristic temperature of coal ash [27,28]. The high-calcium bituminous coal in Inner Mongolia of China has the characteristics of good combustion performance, low ash, low sulfur, and low phosphorus, but its ash melting characteristic temperature is low (below 1,533 K), and the tuyere slagging tendency is large when used in blast furnace injection process [29]. Exploring the law of mineral transformation [30] in the combustion process of high-calcium bituminous coal and the influence of coal ash composition on the liquid production in the melting process is conducive to clarifying the ash melting slag formation mechanism in the combustion process of high-calcium bituminous coal, and laying a theoretical foundation for large-scale injection of high-calcium bituminous coal into blast furnaces.

2 Experiment and calculation

2.1 Experimental materials

The experimental raw material was Shendong high-calcium bituminous coal in Inner Mongolia, China. The raw coal was dried at 378 K and crushed to below 200 meshes.

1 g pulverized coal was weighed and spread on the bottom of 4 porcelain boats, respectively, and the 4 porcelain boats were placed in a vacuum atmosphere furnace. Air was continuously introduced into the furnace, and the heating endpoints were 873, 1,073, 1,273, and 1,473 K, respectively. The furnace was kept for 120 min. After the coal powder turned into ash fully, the porcelain boat with coal ash was quickly removed from the furnace, and the coal ash was poured into the bottom of a steel basin immersed in water. This can avoid long time air cooling, which will change the internal structure of coal ash, but also prevent water quenching caused by porcelain boat burst into water to reduce coal ash yield. According to the national standards (GB/T212-2008, GB/T 31391-2015, and GB/T219-2008) of China, the effect of ash melting temperature on high-calcium bituminous coal were analyzed, using the industrial analysis and elemental analysis, and the results are shown in Tables 1 and 2. It can be seen that high-calcium bituminous coal belongs to both high-calcium coal and high silicon–aluminum ratio coal. The content of Fe_2O_3 in the ash of high-calcium bituminous coal is as high as 22.92%, which belongs to the category of high-iron coal.

2.2 Methods

The phase analysis of ash samples prepared from high-calcium bituminous coal at different temperatures was carried out by using Japan MXP21VAHF X-ray diffractometer (XRD). The experimental radiation target was Cu, and the scanning angle was selected from 10° to 100° .

German Zeiss EVO-18 scanning electron microscope (SEM) was used to analyze the microstructure of high-calcium bituminous coal ash samples at different temperatures. The mineral transformation of ash during combustion of high-calcium pulverized coal was studied. The main parameters include resolution: 3.0 nm (30 kV), 2.0 nm (30 kV), 4.5 nm (30 kV), accelerating voltage: 0.2–30 kV, magnification power: 5–1,000,000.

The VL2000DX type ultra-high temperature confocal microscope with pull-up and compression function was

Table 1: Proximate and ultimate analysis of pulverized coal (wt%)

Description of sample	Proximate analysis			Ultimate analysis				
	V_d	A_d	FC_d	C	H	N	O	S
High-calcium bituminous coal	30.00	7.58	62.42	74.59	3.95	0.76	12.64	0.21

V_d : The yield of volatile organic compounds from high calcium bituminous coal heated in isolated air under specified conditions is called volatile matter. A_d : The solid residue remaining after complete combustion of high calcium bituminous coal is called ash. FC_d : The residue from the char residue after the determination of volatile matter in coal samples minus ash is called fixed carbon.

Table 2: Ash fusion temperature and main chemical composition of coal ash^a

Description of sample	Ash fusion temperature (K)				Main chemical composition of coal ash (wt%)					
	DT	ST	HT	FT	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
High-calcium bituminous coal	1,465	1,503	1,525	1,538	21.17	10.64	22.92	31.70	0.89	8.72

^aDT: deformation temperature; ST: softening temperature; HT: hemisphere temperature; FT: flow temperature.

DT is the temperature at which the tip or edge of the ash cone begins to round or bend. ST is the temperature at which the ash cone is bent until the cone touches the pallet or the ash cone becomes spherical. HT is a gray cone with an approximate hemispherical shape. FT is the temperature at which the ash cone melts and expands into a thin layer with a height of less than 1.5 mm.

used to observe the *in-situ* melting process of high-calcium bituminous coal at high temperature. The temperature system of the experiment is as follows: Temperature rises from room temperature to 473 K at the rate of 323 K·min⁻¹, from 473 to 873 K at the rate of 373 K·min⁻¹, from 873 to 1,673 K at the rate of 323 K·min⁻¹, and then decreases to room temperature at the rate of 373 K·min⁻¹ after holding at 1,673 K for 10 min.

The Equilib module in FactSage software was used to simulate the mineral transformation process of ash during pulverized coal combustion, and the ash melting mechanism was further discussed from the thermodynamic point of view.

The ash samples prepared at 873 K were analyzed by Thermogravimetry/Differential Thermal Analysis (TG-DTA). The temperature range was 773–1,473 K, the heating rate was 283 K·min⁻¹, and the initial mass of ash sample was 5 mg.

3 Experimental results and discussion

3.1 Mineral conversion during pulverized coal combustion

3.1.1 Phase analysis of coal ash at different temperatures

Figure 1 shows the photos of high-calcium bituminous coal prepared at 873, 1,073, 1,273, and 1,473 K. It can be found from the figure that the color of ash samples prepared by the same pulverized coal at different temperatures is different, which is related to the different mineral composition of ash at different temperatures. At the same time, it can be found that the ash of high-calcium bituminous coal ashed at 1,473 K has melted and adhered to the bottom of the porcelain boat, indicating that the ash

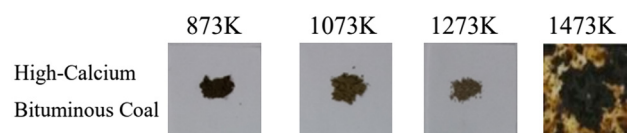
of pulverized coal ashed at 1,473 K has formed a low melting point eutectic. After rapid cooling, slagging adhesion appears on the surface of porcelain boat.

The absorption or reflection of X-ray by minerals in coal ash is different, which is not only related to the mineral content, but also related to the crystal structure of minerals. However, for the same mineral, the change in X-ray diffraction intensity can approximately characterize the change in mineral content [31].

Figure 2 shows the X-ray diffraction patterns of ash samples obtained from high-calcium bituminous coal after ashing at 873, 1,073, 1,273, and 1,473 K. Comparing the XRD results of ash after coal ashing at different temperatures, it can be found that the composition of the ashed samples at 873 K is very different from that at 1,473 K.

In the coal ash after ashing at 873 K, the main mineral components are calcite (CaCO₃), quartz (SiO₂), hematite (Fe₂O₃), and gypsum (CaSO₄). When analyzing and retrieving the phase, it is found that the diffraction peak of E-(Mg_{0.064}Ca_{0.936}) (CO₃) is similar to that of the diffraction peak of A-calcite (CaCO₃). This is because the content of MgO in the ash of high-calcium bituminous coal is only 0.89%. At the same time, the structure of MgCO₃ and CaCO₃ is calculated by Materials Studio, a new generation of material calculation software developed by Accelrys Company in the United States, as shown in Figure 3. It is found that the structure of MgCO₃ and CaCO₃ is consistent, which is ABO₃ structure. Therefore, the Mg atom in the phase is partially doped in the Ca atom position.

With the increase in temperature, carbonate minerals disappear. The main minerals in ash samples ashed at

**Figure 1:** Gray photographs prepared at different temperatures.

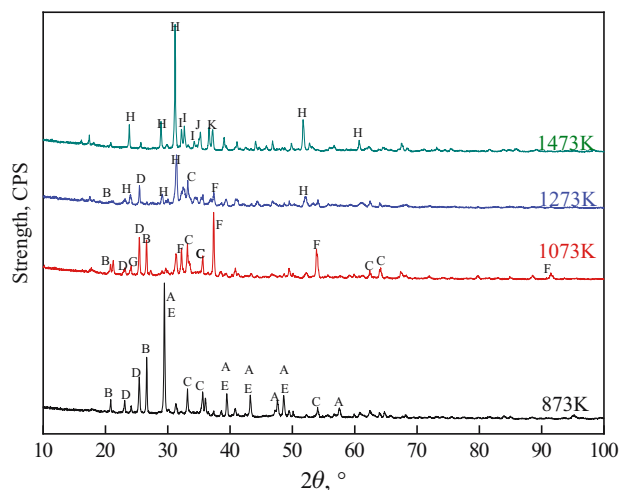


Figure 2: XRD patterns of coal ash after ashing at different temperatures. A – CaCO_3 ; B – SiO_2 ; C – Fe_2O_3 ; D – CaSO_4 ; E – $(\text{Mg}_{0.064}\text{Ca}_{0.936})(\text{CO}_3)$; F – CaO ; G – $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$; H – $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$; I – Ca_2SiO_4 ; J – $\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$; K – $\text{Ca}_2(\text{Mg}_{0.5}\text{Al}_{0.5})(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_7$.

1,073 K are CaO , CaSO_4 , $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$, SiO_2 , and Fe_2O_3 . The decomposition reaction of calcite mainly occurs in the temperature range from 873 to 1,073 K. When other

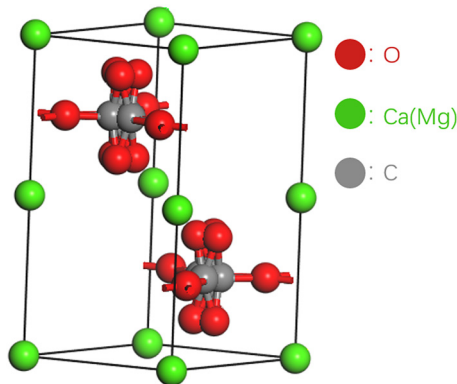
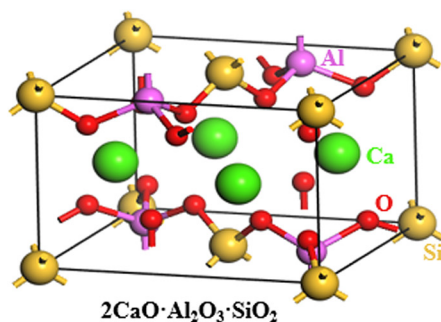
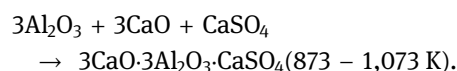
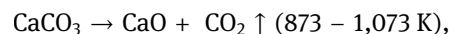


Figure 3: Phase structure of CaCO_3 and MgCO_3 .



minerals exist, the initial decomposition temperature of CaCO_3 will be greatly reduced [32]. During this reaction, the ash weight became smaller due to the escape of decomposition product CO_2 . The more CaO content in the coal ash component, that is, the more CaCO_3 content in low temperature mineral component, this characteristic peak is more obvious. At the same time, due to the appearance of decomposition product CaO , Al_2O_3 will react with gypsum (CaSO_4) and CaO to form calcium aluminate sulfate ($3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$) at about 1,073 K [33]. The mineral transformation process of coal ash at 873–1,073 K is shown as follows.



When the temperature continues to rise, in the temperature range of 1,073–1,273 K, high active SiO_2 reacts with CaO and Al_2O_3 to form a high melting point complex compound calcareous feldspar ($2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$), and the ash is still in the form of solid particles. When searching for the phase, it is found that there are small amounts of diffraction peaks of magnesium akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) overlapping with one of the characteristic peaks of calcium xanthate. Due to the low content of Mg, and the structures of magnesium xanthate and calcium xanthate being similar, as shown in Figure 4, they are all P-421M structure, so $\text{Ca}_2\text{MgSi}_2\text{O}_7$ can be ignored.

It can be seen from Figure 2 that at 1,273 K, the diffraction peak intensity of SiO_2 in ash was very low, and a large number of free SiO_2 were combined with other oxides to transform into a stable chemical state. The main transformation process of minerals in coal ash at 1,073–1,273 K (due to the same structure as $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$, the formation process of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is not considered) is shown as follows:

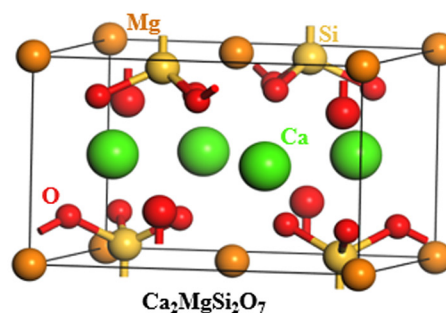
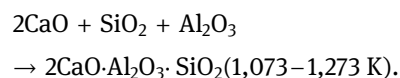


Figure 4: Structure diagram of gehlenite and magnesite.

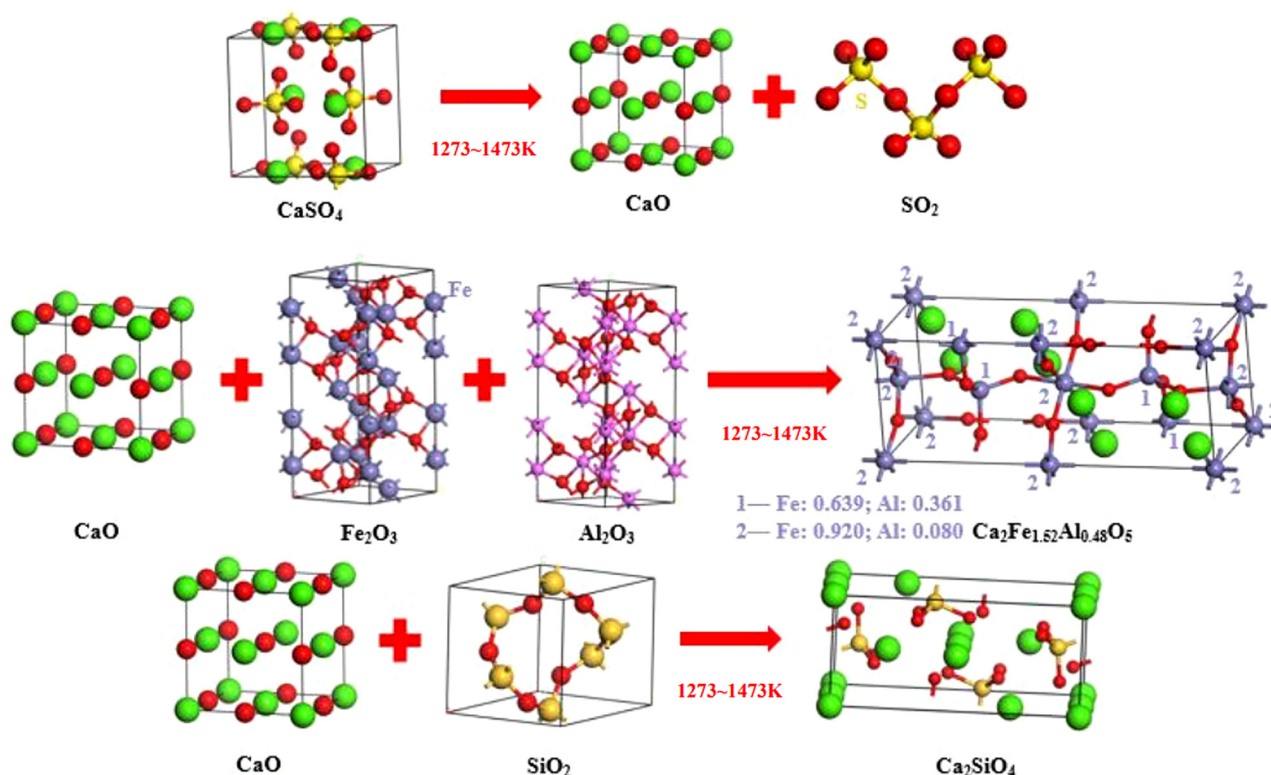


Figure 5: Mineral transformation process at 1,273–1,473 K.

It can be seen from Figure 2 that at 1,473 K, the intensity of the diffraction peak of calcesite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) increases, the complex compound $\text{Ca}_2(\text{Mg}_{0.5}\text{Al}_{0.5})\text{O}_7$ ($\text{Si}_{1.5}\text{Al}_{0.5}\text{O}_7$) doped with Mg forms, the diffraction peaks of CaSO_4 , SiO_2 , and Fe_2O_3 disappear, and the diffraction peaks of plagioclase (Ca_2SiO_4) and perovskite ($\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$) appear. The disappearance of CaSO_4 diffraction peak indicates that anhydrite decomposes in the temperature range of 1,273–1,473 K. The decomposition product CaO reacts with free Al_2O_3 and Fe_2O_3 in the system to form a complex compound perovskite ($\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$). At the same time, CaO reacts with SiO_2 to form a larnite (Ca_2SiO_4) in the temperature range of 1,273–1,473 K. Figure 5 is the main transformation process of minerals in coal ash at 1,273–1,473 K.

It can be seen from Figure 5 that the CaO generated by CaSO_4 decomposition is mainly used to participate in the reaction of the formation of larnite (Ca_2SiO_4) and calcium ferroalumina ($\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$). In the structure of calcium ferroalumina, Fe and Al are doped with each other, and the doping ratios at position 1 and 2 are different, 0.639:0.631 and 0.920:0.080, respectively. The reason for the different doping ratios is that the number of oxygen atoms connected by at positions 1 and 2 is different, which is 4 and 6, respectively. Due to the complexity

and instability of the structures of $\text{Ca}_2(\text{Mg}_{0.5}\text{Al}_{0.5})\text{O}_7$ and $\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$, their melting points are low. When they reach the melting state at 1,473 K, they will dissolve with $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and Ca_2SiO_4 , resulting in agglomeration and sintering.

3.1.2 Microstructure analysis of coal ash at different temperatures

The SEM images of ash samples obtained from high-calcium bituminous coal ashing at 873, 1,073, 1,273, and 1,473 K are shown in Figure 6.

Any system has a tendency to change from high-energy state to low-energy state spontaneously. Compared with the bulk structure, the small spherical particles are in an unstable state with high-energy, and have the tendency of reducing the surface area and leaving the surface to reach the thermodynamic stable state. Small spherical particles contact each other in the form of point contact, with large specific surface area and high specific surface area energy. When the temperature increases to a certain extent, the mobility of atoms (ions) increases, and the particles will deform to a certain extent. The contact area between the particles increases, and the surface energy is

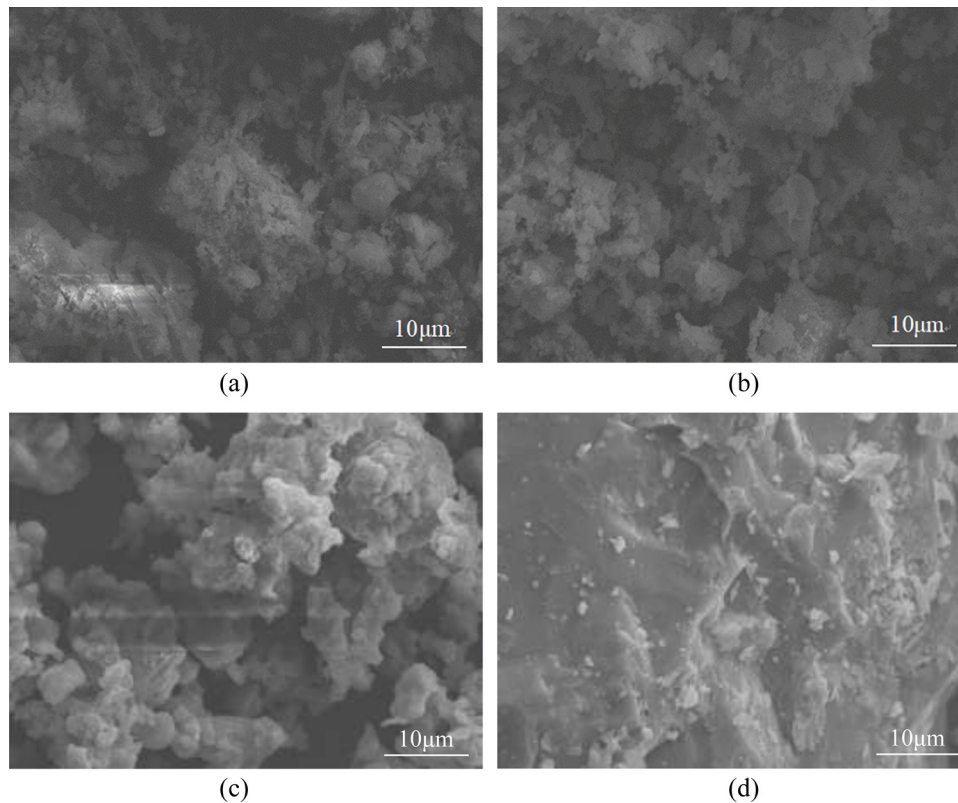


Figure 6: Micromorphology of ashed samples at different temperatures: (a) 873 K, (b) 1,073 K, (c) 1,273 K, and (d) 1,473 K.

released and the particles are sintered. Therefore, temperature is the driving force for the sintering process.

It can be seen from Figure 6 that during the ashing process at 873 K, the CO_2 , H_2O , and other gases generated by the oxidation reaction of fixed carbon and organic matter in the pulverized coal particles with oxygen will be released from the inside of the particles, forming a loose porous structure on the surface of the particles. At the same time, the raw minerals in coal react, the mineral crystal and residual carbon fiber gradually disappear, the pore on the particle surface shrinks, the particle structure of coal ash is gradually close, and the ash sample is flocculent. During the ashing process at 1,073 K, due to the decomposition of a large amount of CaCO_3 in the ash, CO_2 escaped, and the specific surface area of the flocculent agglomeration of the ash sample increased. At the same time, a small amount of spherical particles appeared, indicating that the ash particles began to agglomerate in the temperature range of 873–1,073 K. It can be seen from the photos of the samples ashed at 1,273 K that there are a large number of spherical particles, and the agglomeration between ash particles is closer, which is due to the higher energy of particles at higher temperatures, and more inclined to exist in a stable spherical structure. At the same time, it can be found that some spherical particles

deform, and the contact area between them increases. The surface energy is released and the combination between aggregates occurs. The traces of liquid flow can be observed on the structural surface formed by sintering. Almost all the particles have melted and combined together, and the surface of the block structure has pores of different sizes and is flat and smooth. It can be seen from the photos of the samples obtained by ashing at 1,473 K that the sintering behavior between different minerals in ash is obvious, and the number of pores on the surface decreases and becomes extremely dense and smooth. Combined with the results of XRD analysis, the complex low melting point compound $\text{Ca}_2\text{Fe}_{1.52}\text{Al}_{0.48}\text{O}_5$ was formed by the decomposition of anhydrite at 1,273–1,473 K and the reaction with Fe_2O_3 and Al_2O_3 . At the same time, other complex compounds $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, Ca_2SiO_4 , and $\text{Ca}_2(\text{Mg}_{0.5}\text{Al}_{0.5}) (\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_7$ were found in the system. The complex compounds were mutually soluble, the degree of ash melting was increased, and the mineral particles were seriously agglomerated and sintered. The sintered surface was smooth and dense.

The high-temperature melting process of ash samples prepared from high-calcium bituminous coal at 873 K was observed by VL2000DX type ultra-high temperature confocal microscope with tensile-compression function.

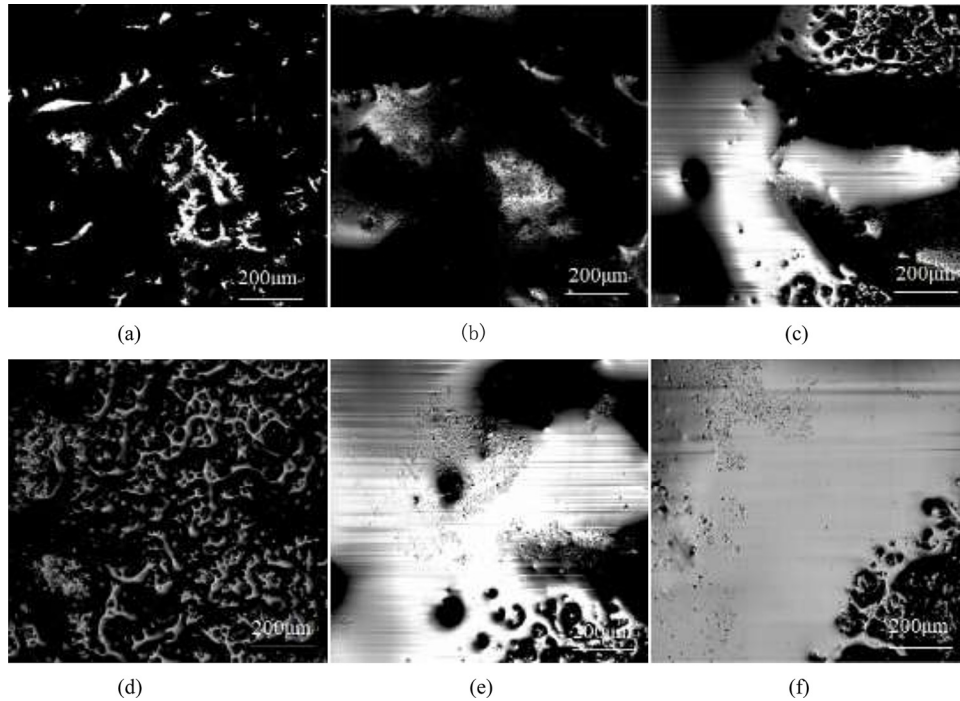


Figure 7: High temperature melting process of coal ash. (a) 1,423 K, (b) 1,473 K, (c) 1,523 K, (d) 1,573 K, (e) 1,623 K, and (f) 1,673 K.

The high-temperature hot stage images of ash melt at different temperatures are shown in Figure 7. It can be seen from the diagram that the ash sample begins to shrink and melt at 1,423 K. With the increase in temperature to 1,473 K, the degree of melting increases, and the low melting point compounds are melted to form liquid slag. With the increase in temperature, the amount of liquid phase increases. Between 1,523 and 1,573 K, a large amount of liquid phase is generated, the surface of the melt boils, and the liquid phase dispersion distribution. With the increase in temperature, due to the molten slag, the high melting point compounds and the low melting point compounds are eutectic [34], and slowly dissolve into the liquid phase. In the temperature range of 1,623–1,673 K, the high melting point compounds and the liquid phase are fully eutectic. The slag gradually becomes homogeneous.

3.1.3 TG analysis of coal ash at 873 K

The TG curve of pulverized coal combustion reaction is affected by its volatile analysis and fixed carbon combustion, which cannot clearly reflect the mineral transformation law of pulverized coal combustion process. In order to eliminate the influence of volatile analysis and fixed carbon combustion, the ash samples of high-calcium bituminous coal ashed at 873 K were analyzed by TG-DTA, and the characteristic peak distribution of TG-DTA

curve was observed. According to the results of coal ash phase analysis in the previous part, the causes of weight loss and DTA peak were analyzed. Figure 8 shows the TG-DTA curves of ash samples after coal ashing at 873 K.

It can be seen from the figure that in the temperature range of 873–993 K, the ash sample had obvious weight loss, which was due to the decomposition of CaCO_3 in this temperature range, the escape of CO_2 , and the weight loss of the sample. At the same time, there is also a weight loss peak in the temperature range of 1,373–1,473 K, which just verifies the analysis and inference of CaSO_4 decomposition in this temperature range.

3.2 Effect of composition on liquid phase formation in coal ash melting process

The melting process of coal ash is a high-temperature reaction process. The melting characteristics of coal ash are closely related to the behavior of minerals and the chemical reactions between minerals in the melting process. In order to better explain the influence of ash composition on coal ash melting characteristics, FactSage thermodynamic calculation software was used to simulate and calculate the heating process of coal ash with different components, and the influence of components on mineral transformation in coal ash melting process was explored.

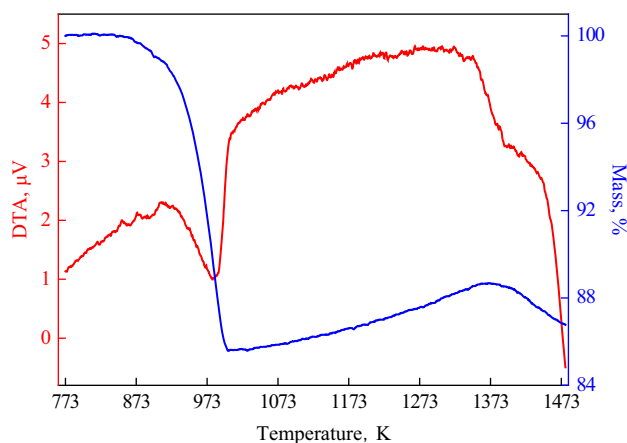


Figure 8: DTA-TG curves of samples after ashing at 873 K.

In order to study the effect of the components on mineral transformation during ash fusion, Fact, Fact53, and FToxid databases were used to calculate the ash composition of high-calcium bituminous coal. In the calculation, without adding gas and other substances, the temperature was set as a variable to study the change in minerals in the process of ash rising from 873 to 1,873 K, and the temperature interval was 373 K. Setting the content of a certain oxide as a variable, the influence of different oxides on the liquid production in ash at a specific temperature was studied. According to the calculation results, the influence of different oxides in ash on the melting characteristics of coal ash was analyzed.

3.2.1 Effect of CaO content on formation of ash liquid phase CaO

In order to study the effect of CaO content in ash on the melting characteristics of coal ash, based on the ash composition of high-calcium bituminous coal, the content of CaO in ash was changed, and the relative content of other components was unchanged. The design CaO content was changed from 20.00 to 40.00%, and the ash mass was set to 100 g. The change in CaO content under

different temperature conditions was calculated, and the effect of CaO content on liquid production at corresponding temperature was calculated. The composition of each group is shown in Table 3. Figure 9 is the relationship between temperature and ash liquid production. It can be seen from the figure that no matter how the CaO component content changes, the liquid production increases with the increase in the temperature, and the liquid content in ash reaches 100% at 1,673 K, and there is no solid phase. At the same time, it can be seen from the figure that when the CaO content was 20.00–25.00%, a small amount of liquid phase began to form in the ash at 873 K. When the CaO content was 31.70%, the liquid phase began to form at 973 K; when the CaO content was 35.00%, the liquid phase began to form at 1,073 K; when the CaO content was 40.00%, the liquid phase formation temperature is higher, and it starts to form above 1,373 K, but the production increases rapidly. CaO, as the active carrier of oxygen during coal combustion, promotes the diffusion of oxygen from the gas phase to the carbon surface, effectively increases the activity of the reaction surface of pulverized coal, thereby reducing the ignition temperature of the fixed carbon surface, which is conducive to the fracture of alkyl side chains of aliphatic hydrocarbons and aromatic hydrocarbons and the precipitation of gas products. Under the condition of different CaO contents, there is a small amount of liquid phase formation at 873 K. With the increase in the temperature, the liquid phase increases. When the temperature reaches 1,473 K, the liquid volume increases rapidly. When the temperature reaches 1,673 K, the curve changes smoothly, and there is no solid phase at this time. It shows that the CaO content affects the starting temperature of ash liquid phase. The higher the CaO content, the higher the starting temperature of liquid phase in ash. Increasing the CaO content is beneficial to control the liquid phase formation of ash in the temperature range of 1,473–1,573 K.

Figure 10 is the relationship between CaO content and liquid phase formation in ash at different temperatures. As shown in Figure 10, the liquid phase formation in ash decreases with the increase in the CaO content at 1,273–1,373 K.

Table 3: Ash composition of different CaO content (wt%)

Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	other
Ash 1	21.17	10.64	22.92	31.70	0.89	8.72	1.07	1.35	1.54
Ash 2	24.80	12.46	26.85	20.00	1.04	10.21	1.25	1.58	1.81
Ash 3	23.25	11.68	25.17	25.00	0.98	9.58	1.17	1.48	1.69
Ash 4	20.15	10.12	21.81	35.00	0.85	8.30	1.02	1.28	1.47
Ash 5	18.60	9.35	20.13	40.00	0.78	7.66	0.94	1.19	1.35

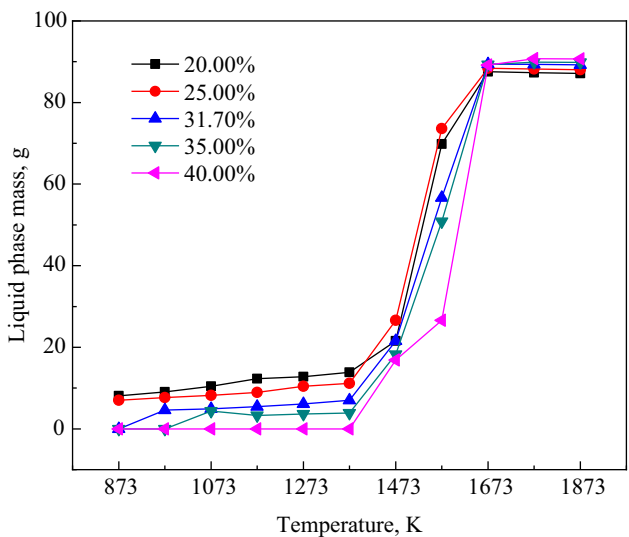


Figure 9: Relationship between liquid production and temperature under different CaO contents.

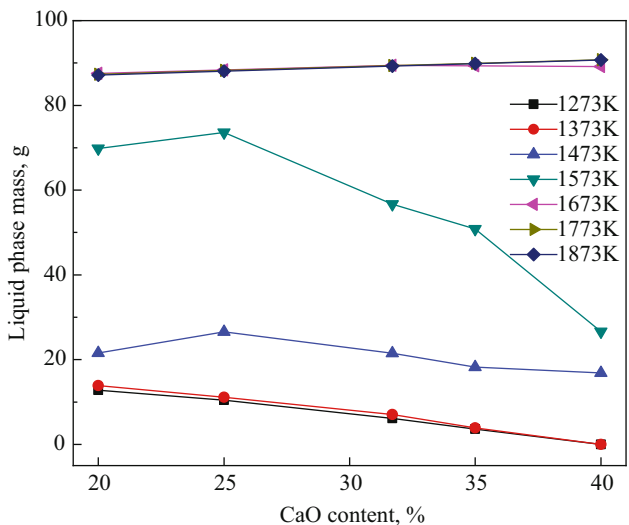


Figure 10: Relationship between liquid production and CaO content at different temperatures.

In the temperature range of 1,473–1,573 K, with the increase in the CaO content, the liquid production in ash increases first and then decreases. In other words, in the

temperature range of 1,473–1,573 K, the increase in the CaO content within a certain range has an increasing effect on the liquid production of ash, and the liquid production decreases when the CaO content continues to increase. In the temperature range of 1,673–1,873 K, with the increase in the CaO content, liquid production increases. Therefore, the effect of CaO on liquid phase formation of ash is different at different temperatures. The higher the temperature, the higher the content of CaO, and the more liquid production in ash.

3.2.2 Effect of Fe_2O_3 content on liquid phase formation of ash

In order to study the influence of Fe_2O_3 content in ash on the ash fusion characteristics, the ash composition of high-calcium bituminous coal was taken as the benchmark, and the content of Fe_2O_3 in ash was changed. The relative contents of other components were unchanged. The content of Fe_2O_3 was designed to change from 13.00 to 33.00%, and the ash mass was set to 100 g. The change in Fe_2O_3 content under different temperature conditions was calculated, and the influence on the liquid production at corresponding temperature was calculated. The composition of each group is shown in Table 4.

Figure 11 is the relationship between temperature and ash liquid production. It can be seen from the figure that no matter how the content of Fe_2O_3 component changes, the liquid production increases with the increase in temperature, and the liquid content in ash reaches 100% at 1,673 K, without solid phase. At the same time, it can be seen from the figure that when the Fe_2O_3 content was 13.00 and 22.92%, a small amount of liquid phase began to appear in the ash at 973 K. When the content of Fe_2O_3 was between 18.00 and 28.00%, the liquid phase in ash began to form at about 1,073 K. When the Fe_2O_3 content was 33.00%, the liquid phase starts to form at 1,173 K. When the temperature is above 1,173 K, there is little difference in the increasing trend of liquid phase formation under different temperature conditions, so the content of

Table 4: Ash composition of different Fe_2O_3 contents (wt%)

Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Other
Ash 1	21.17	10.64	22.92	31.70	0.89	8.72	1.07	1.35	1.54
Ash 2	23.90	12.01	13.00	35.78	1.00	9.84	1.21	1.52	1.74
Ash 3	22.52	11.32	18.00	33.72	0.95	9.28	1.14	1.44	1.63
Ash 4	19.77	9.94	28.00	29.61	0.83	8.15	1.00	1.26	1.44
Ash 5	18.40	9.25	33.00	27.55	0.77	7.58	0.93	1.17	1.35

Fe_2O_3 has little effect on the temperature of liquid phase formation of ash.

Figure 12 shows the relationship between Fe_2O_3 content and liquid phase yield in ash at different temperatures. As shown in the figure, between 1,273 and 1,373 K,

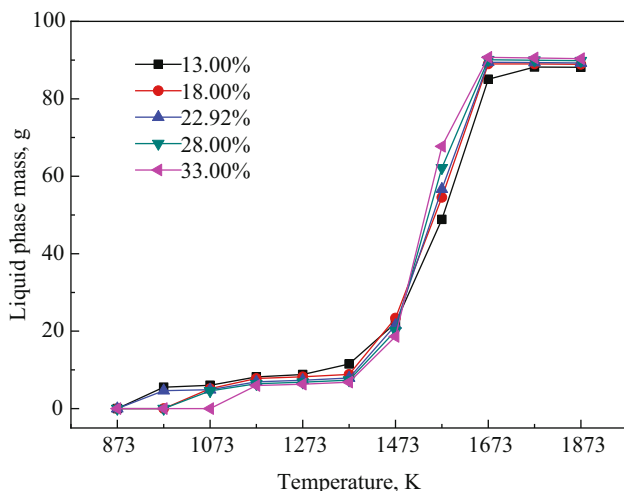


Figure 11: Relationship between liquid production and temperature under different Fe_2O_3 contents.

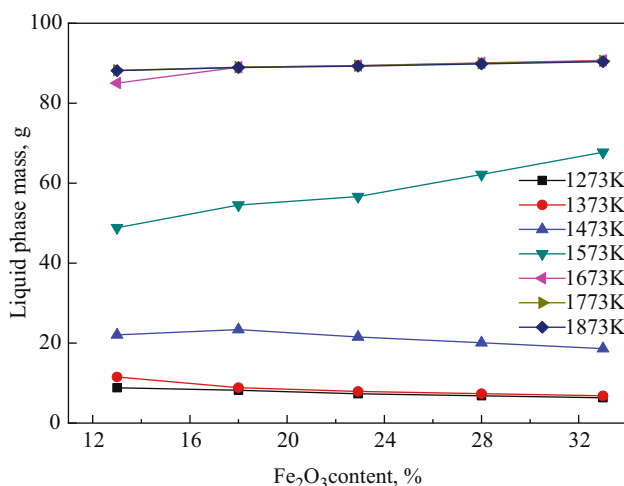


Figure 12: Relationship between liquid production and Fe_2O_3 content at different temperatures.

with the increase in the Fe_2O_3 content, the amount of liquid phase in ash decreases. However, after the Fe_2O_3 content increases to 22.92%, with the increase in the Fe_2O_3 content, the amount of liquid phase in ash decreases. At 1,473 K, with the increase in the Fe_2O_3 content, the liquid production in ash increased first and then decreased. In other words, at 1,573 K, the increase in the Fe_2O_3 content within a certain range increased the liquid production of ash, and the liquid production decreased after the increase in the Fe_2O_3 . In the temperature range of 1,573–1,873 K, with the increase in the Fe_2O_3 content, the liquid production increased. However, when the temperature reached above 1,673 K, when the Fe_2O_3 content increased to 18.00%, the increase in the liquid production in ash decreased greatly and remained basically unchanged.

Therefore, the effect of Fe_2O_3 content on the liquid phase formation of ash is different at different temperatures. The effect of Fe_2O_3 content on the liquid phase formation of ash is obvious at 1,473 K. When the Fe_2O_3 content is lower than 18.00%, the amount of liquid phase in ash increases with the increase in the Fe_2O_3 content at high temperature. When the temperature reaches 1,573 K, Fe_2O_3 promotes ash liquid phase formation. At the same time, Fe_2O_3 can reduce the temperature of coal ash in a weak reduction atmosphere.

3.2.3 Effect of Al_2O_3 content on liquid phase formation of ash

In order to study the influence of Al_2O_3 content in ash on the ash fusion characteristics, the ash composition of high-calcium bituminous coal was taken as the benchmark, and the Al_2O_3 content in ash was changed. The relative contents of other components were unchanged. The Al_2O_3 content was designed to change from 5.00 to 25.00%, and the ash mass was set to 100 g. The change in Al_2O_3 content under different temperature conditions was calculated, and the influence on the liquid production at corresponding temperature was calculated. The composition of each group is shown in Table 5.

Table 5: Ash composition of different Al_2O_3 contents (wt%)

Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	other
Ash 1	21.17	10.64	22.92	31.70	0.89	8.72	1.07	1.35	1.54
Ash 2	22.51	5.00	24.37	33.70	0.95	9.27	1.14	1.44	1.62
Ash 3	20.14	15.00	21.80	30.15	0.85	8.29	1.02	1.28	1.47
Ash 4	18.95	20.00	20.52	28.38	0.80	7.81	0.96	1.21	1.37
Ash 5	17.77	25.00	19.24	26.61	0.75	7.32	0.90	1.13	1.28

Figure 13 shows the relationship between temperature and ash liquid phase production. It can be seen from the figure that no matter how the Al_2O_3 composition content changes, the liquid phase production increases with the increase in the temperature, but according to the phase equilibrium calculation results, When the content of Al_2O_3 is greater than 15.00%, only when the temperature is higher than 1,773 K, the ash will be 100% pure liquid and there will be no solid phase. At the same time, it can be seen from the figure that when the Al_2O_3 content is 20.00% and the temperature is 873 K, a small amount of liquid phase is formed in the ash. When the Al_2O_3 content was between 10.64 and 25.00%, a small amount of liquid phase began to appear in the ash at 973 K. When the Al_2O_3 content was between 5.00 and 15.00%, the liquid phase in the ash began to form at about 1,073 K. There was no obvious regularity between the Al_2O_3 content and the initial formation temperature of the liquid phase, indicating that the Al_2O_3 content had little effect on the initial formation temperature of the ash liquid phase. At 1,673 K, when the content of Al_2O_3 is 15.00, 20.00, and 30.00%, there are high melting point compounds in ash in addition to liquid phase in the form of solid phase, and with the increase in Al_2O_3 content, liquid phase formation decreases in turn, indicating that increasing the content of Al_2O_3 is beneficial to improve the melting characteristics of ash at 1,673 K. Increasing Al_2O_3 content can reduce the temperature range of ash liquid phase formation to 1,473–1,673 K, and Al_2O_3 has obvious effect on increasing temperature.

The relationship between Al_2O_3 content and liquid phase formation in ash at different temperatures is shown in Figure 14. At 1,273–1,373 K, with the increase in Al_2O_3

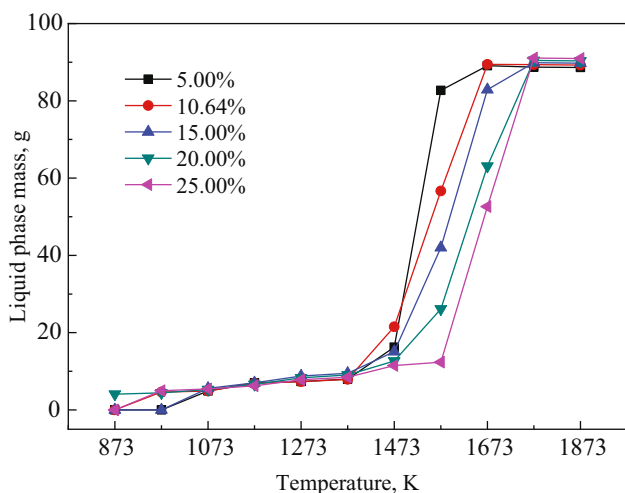


Figure 13: Relationship between liquid production and temperature under different Al_2O_3 contents.

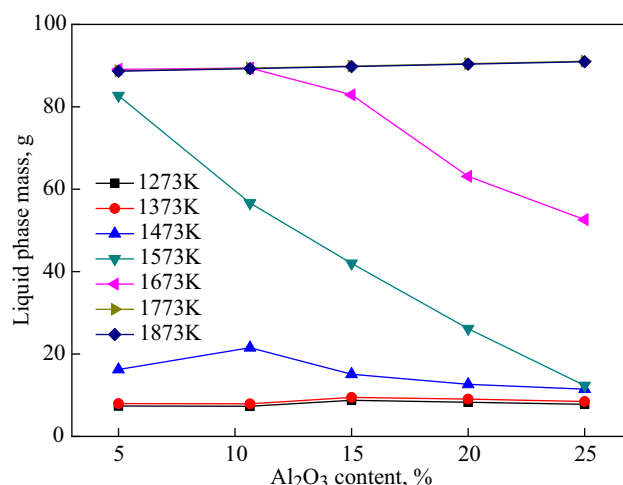


Figure 14: Relationship between liquid production and Al_2O_3 content at different temperatures.

content, the liquid phase formation in ash increased slightly but basically changed little. At 1,473 K, with the increase in Al_2O_3 content, the liquid production in ash increases first and then decreases. That is to say, at 1,473 K, the increase in Al_2O_3 content within a certain range has an increasing effect on the liquid production of ash, and the liquid production decreases when the Al_2O_3 content continues to increase. In the temperature range of 1,573–1,673 K, the amount of liquid phase decreases with the increase in Al_2O_3 content. In the temperature range of 1,773–1,873 K, the increase in Al_2O_3 content has no obvious effect on the liquid production. Therefore, increasing Al_2O_3 content in the temperature range of 1,573–1,673 K can obviously improve the melting characteristics of ash.

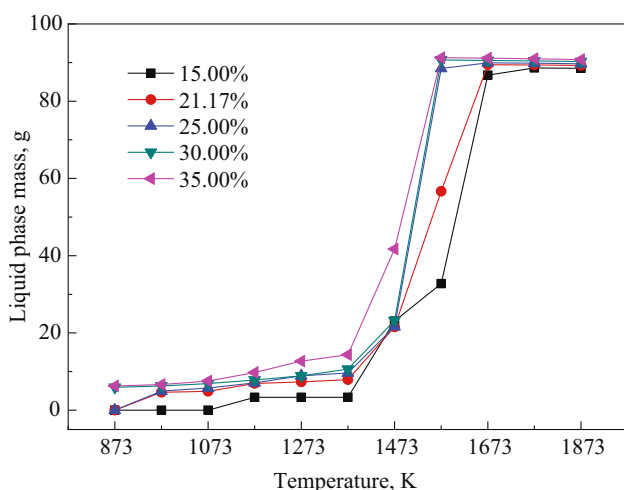
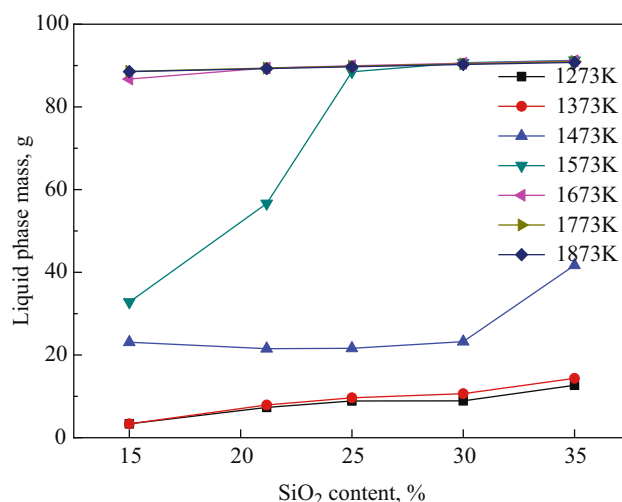
3.2.4 Effect of SiO_2 content on liquid phase formation of ash

In order to study the influence of SiO_2 content in ash on the ash fusion characteristics, the ash composition of high-calcium bituminous coal was taken as the benchmark, and the SiO_2 content in ash was changed. The relative contents of other components were unchanged. The SiO_2 content was designed to change from 15.00 to 35.00%, and the ash mass was set to 100 g. The change in SiO_2 content under different temperature conditions was calculated, and the influence on the liquid production at corresponding temperature was calculated. The components of each group are shown in Table 6.

As shown in Figure 15, the relationship between temperature and liquid phase formation of ash can be seen from the figure that no matter how the content of SiO_2

Table 6: Ash composition of different SiO₂ content (wt%)

Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Other
Ash 1	21.17	10.64	22.92	31.70	0.89	8.72	1.07	1.35	1.54
Ash 2	15.00	11.47	24.71	34.18	0.96	9.40	1.15	1.46	1.67
Ash 3	25.00	10.12	21.80	30.16	0.85	8.30	1.02	1.28	1.47
Ash 4	30.00	9.45	20.35	28.15	0.79	7.74	0.95	1.20	1.37
Ash 5	35.00	8.77	18.90	26.14	0.73	7.19	0.88	1.11	1.28

**Figure 15:** Relationship between liquid production and temperature under different SiO₂ contents.**Figure 16:** Relationship between liquid production and SiO₂ content at different temperatures.

component changes, the liquid phase formation increases with the increase in the temperature, but the initial formation temperature of liquid phase is different under different SiO₂ content: when the SiO₂ content was 15.00%, no liquid phase is formed in ash at 873–1,073 K; when the SiO₂ content was 15.00–21.17%, a small amount of liquid phase began to form in the ash at 973 K. When SiO₂ content was more than 25.00%, liquid phase appears in ash at 873 K. At the same time, it can be seen from the diagram that when the SiO₂ content is greater than 25.00%, the ash is changed into pure liquid phase at 1,573 K. Therefore, the SiO₂ content affects the starting temperature of liquid phase in ash. The higher the SiO₂ content is, the lower the starting temperature of the liquid phase in ash is.

Figure 16 is the relationship between the SiO₂ content and liquid phase formation in ash at different temperatures. As shown in the figure, in the temperature range of 1,273–1,873 K, with the increase in the SiO₂ content, the amount of liquid phase formation in ash increases, especially at 1,573 K. This is due to the Si-O bond is the necessary structural unit for the formation of low melting point compounds in ash. Therefore, the higher the SiO₂ content

in ash, the more the liquid phase formed at a certain temperature, and the worse the melting characteristics of coal ash.

4 Conclusion

(1) The main mineral transformation in ash is carried out around the different deposition forms of Ca and Si, and calcite decomposition occurs mainly at 873–1,073 K. After the temperature reached 1,073 K, calcite began to form in the ash; when the temperature reaches 1,273 K, the anhydrite in the ash begins to decompose, and the complex compounds such as calcium iron aluminates are formed. Due to the low melting point of the complex compounds formed by atomic doping, the ash has obvious melting slagging phenomenon.

(2) The melting behavior of ash gradually occurs with the change in the morphology. Under different temperature conditions, the morphology of ash is different. With the increase in the temperature, the flocculent agglomeration state of ash sample at 873 K gradually

changes to the flocculent agglomeration state of large specific surface area at 1,073 K, and then gradually sintered to the dense melting state at 1,473 K. The high temperature melting behavior of ash undergoes the process of liquid boiling to liquid fusion.

(3) The formation of liquid phase in ash is the essential reason for its melting behavior. The contents of CaO and SiO₂ affect the starting temperature of liquid phase in ash. The higher the content of CaO, the higher the starting temperature of the liquid phase formation. When the CaO content is 40.00%, the starting temperature of liquid phase is 1,373 K. The higher the content of SiO₂, the lower the starting temperature of the liquid phase formation. When the SiO₂ content is greater than 25.00%, the liquid phase of ash begins to form at 873 K.

(4) Increasing CaO and Al₂O₃ content is conducive to controlling the liquid phase formation of ash in the temperature range of 1,473–1,573 K, and increasing Al₂O₃ content can expand the temperature range of reducing the liquid phase formation of ash to 1,473–1,673 K. The effect of Fe₂O₃ on the liquid phase formation of ash is different at different temperatures. At 1,473 K, with the increase in the Fe₂O₃ content, the liquid phase formation in ash increases first and then decreases, and the critical content is 18.00%. When the temperature reaches 1,573 K and above, Fe₂O₃ promotes the liquid phase formation of ash. The higher the content of SiO₂, the more the liquid phase formed at a certain temperature, and the worse the melting characteristics of coal ash.

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