ABSTRACT: The primary aim of this study is to understand the effect of metal oxide flux on the fusibility of high-calcium coal ash. Based on the decomposition rate, the evolution of mineral matters in high-calcium coal has been investigated. The ash fusion temperatures of samples are measured by adding different flux Al2O3, Na2O, K2O, MgO, and TiO2. The results show that Na2O is the most effective in lowering ash fusion temperatures and its flow temperature could be 110 °C lower than that of the original ash. FactSage is used to calculate the proportion of solid phase and the mineral compositions as a function of the ash compositions and temperature. With the increase of Na2O, mineral matters with a low melting point form in the mixture. Furthermore, the decomposition rate of mineral matters increases in the first stage. The phase diagrams and relative mineral variation illustrate that the mineral and the decomposition rate variations are the main reasons for the change of ash fusion temperatures.

1. INTRODUCTION

As a competitive and promising gasification technology, entrained-flow gasification has been widely applied to produce syngas (CO and H2) in China.1 Coal, as the important feedstock for gasification and the petrochemical industry, will be relied on for a long time. In the entrained-flow gasifier, coal is burned into ash at high temperatures.2 Then, the ash is converted to slag, which flows downward under gravity. Ash fusibility is a significant parameter for entrained-flow gasifiers. It is conventionally represented by the initial deformation temperature (DT), spherical temperature (ST), hemispherical temperature (HT), and ash flow temperature (FT).3 The FT demonstrates the minimum temperature for the ash flowing in the gasifier. In general, the operation temperature of an entrained-flow gasifier is usually 50–200 °C above the FT. The operation temperature directly affects the flow behavior of coal ash in gasification.4 Besides, it ensures the smooth slag tapping, which is crucial for economical and stable run of the gasifier.5 Compared to the high cost and time-consuming viscosity measurements, the ash fusibility test is commonly used in industry for its shortcut, fast speed, and easy operation.

The chemical and physical properties of coals influence the operation of an entrained-flow gasifier.7 High-calcium coals are widely distributed in Xinjiang Uygur Autonomous Region of China. The feature of high-calcium coal is attributed to relatively high CaO contents (higher than 30%), high concentrations of basic oxides, and high AFT. The FT of the high-calcium coal is usually higher than 1300 °C.6 However, the FT is preferred to be below 1300 °C in order to lower the operation cost of the gasifier. Therefore, an effective method is to blend feedstock with flux to decrease the FT of high-calcium coals. For the application of high-calcium coal, it is necessary to study the effect of flux on the ash fusibility of high-calcium coal.

Many investigations have been conducted on the ash fusibility of coals.10–13 van Dyk JC investigated the influence of acidic components on ash FT.14 Huggins used ternary phase diagrams to analyze the influences of CaO, K2CO3, and Fe2O3 on fusion temperature of coal ash.15 Liu studied the relationship between ash fusion temperature and ash composition.16 Kong focused on the relationship between ash content and ash fusion characteristics of Shanxi high-calcium coals.17 However, the effect of different flux on ash fusibility of high-calcium coal has little been reported. The decomposition rate is related to the change of AFT. From the perspective of decomposition rate, the evolution of mineral matters in high-calcium coal has been researched in this study.

The aim of this work is to find the optimal flux for high-calcium coal to lower the operation temperature. The MgO, Al2O3, Na2O, K2O, and TiO2 were added into the high-calcium coal to prepare samples. The ash fusion temperatures were determined. The software package FactSage 7.0 was used to calculate the proportions of the liquid and solid phases, and
mineral compositions as a function of temperature. The relations between AFTs and mineral matters were also illustrated by the phase diagrams.

2. RESULTS AND DISCUSSION

In this experiment, the effects of different flux Al2O3, Na2O, K2O, MgO, and TiO2 on ash fusibility of high-calcium coal were studied. To discover the effect of basic oxide on high-calcium coal AFT, MgO was added into the samples. Taking the base to acid ratio \( \frac{\text{[(Fe2O3+CaO + MgO + Na2O + K2O)}/(SiO2+Al2O3+TiO2)]} {\text{[(Fe2O3+CaO + MgO + Na2O + K2O)}/(SiO2+Al2O3+TiO2)]} \) into account, the effect of Al2O3 on fusibility of high-calcium coal was investigated. Moreover, the effect of low content oxides Na2O, K2O, and TiO2 on fusibility of high-calcium coal was discovered.

2.1. Effect of MgO on AFTs of Coal Samples. MgO is a basic oxide in coal ash. Generally, MgO could decrease AFT and improve flowability of ash samples. As shown in Figure 1, the AFTs of coal samples increase with increasing MgO content when its content in the original coal ash is above 10%. When the MgO content is 30%, the FT is 1550 °C. It demonstrates that MgO exhibits a negative effect on the AFT of the SX sample. That is to say, excessive basic oxides in coal ash could increase the AFT.

Figure 2 presents the coal ash composition with different MgO contents and the liquidus temperatures for an S/A mole ratio of 2.35 and a CaO/FeO mole ratio of 1.69. The diverse color curves in Figure 2 indicate different liquidus temperatures in distinct phases. The points represent the chemical compositions of the blended ashes with different MgO contents. The first point in the top left corner is chemical compositions of SX coal ash, and MgO content is 10.12% (wt). It is located in the monoxide primary phase field. With the MgO content increasing, the chemical compositions of the blended ashes move to the MgO corner along the straight line. The liquidus temperature increases with the increase of MgO content. When MgO content is 10.12%, the liquidus temperature of the ash sample is about 1250 °C. However, when the MgO content is 20%, the liquidus temperature of the sample is about 1390 °C. The trend revealed in the phase diagram agrees with the AFT results.

The relative mineral mass in coal ash with MgO contents of 15, 20, and 30% at different temperatures is displayed in Figure 3. The primary phase does not change with the increasing MgO content. However, the liquidus temperature increases from 1900 to 2400 °C with the MgO content increasing from 15 to 30%. It shows that the composition of mineral and the decomposition rate of mineral are closely related to the AFT.

The decomposition rate of mineral can be expressed as: the mineral mass/(liquidus temperature−solid temperature). The mineral matters are easy to fuse at a faster decomposition rate.
The decomposition rate of minerals decrease as the MgO content increases. For example, the decomposition rate of mineral matters is 100/1200% °C, when the content of MgO is 15%. The decomposition rate of mineral matters is 100/1400% °C, when the content of MgO reaches 20%. For the sample with 30% MgO, the decomposition rate of mineral matters is 100/1600% °C. With the decreasing decomposition rate of mineral matters, the fusion temperature of the sample increases. The mentioned explanations may account for the results that AFTs increase with the increasing MgO content.

2.2. Effect of Al2O3 on AFTs of Coal Samples. The content of the basic component is higher than 68% in SX coal ash. Thus, Al2O3 is an acid additive that is used to decrease the AFTs of SX coal ash. As shown in Figure 4, the AFTs drop as the Al2O3 content increases until the Al2O3 content reaches 10%. With the content of Al2O3 continuing to increase, the AFTs increase sharply. It is obvious that the FT reaches the minimum 1335 °C, which is 51 °C lower than that of SX coal. Obviously, Al2O3 could decrease the AFTs to a certain extent.

The pseudoternary phase diagram of an SiO2−Al2O3−CaO−FeO system is illustrated in Figure 5. It expresses the phase transition with a CaO/FeO mole ratio of 1.69 as a function of Al2O3 content. The first point in the top right corner is the chemical compositions of SX coal ash, and the Al2O3 content is 7.88% (wt). It is located in the Ca2SiO4 primary phase field. As the Al2O3 content increases, the chemical compositions of blended ashes move to the Al2O3 corner along the straight line. When the chemical compositions of the ashes are located in the Ca2Al2SiO7 primary field, the liquidus temperature decreases. As the Al2O3 content continues to increase, it moves into the CaAl2SiO7 primary phase field. The liquidus temperature increases with excessive Al2O3. When Al2O3 content is 10%, the liquidus temperature of the sample is about 1290 °C. However, when Al2O3 content is 18%, the liquidus temperature of sample is about 1380 °C. When the Al2O3 content continues to increase, the liquidus temperature of the sample increases. The trend revealed in the phase diagram is similar to the AFT results.

The relative mineral mass in the SiO2−Al2O3−CaO−FeO−MgO−Na2O−K2O−TiO2 system is calculated by FactSage. Figure 6 displays the relative mineral mass with Al2O3 contents of 10, 20, and 30%. It indicates that the liquidus temperature increases from 1900 to 2100 °C when the Al2O3 content increases from 10 to 30%. In addition, the decomposition rate of mineral matters decreases with the increase of Al2O3 content. For example, the decomposition rate of mineral matters is 100/1000% °C, when the content of Al2O3 is 10%. With the content of Al2O3 increasing to 20%, the decomposition rate of mineral matters is 100/1200° C. The decomposition rate of mineral matters is 100/1400% °C, when the content of Al2O3 increases to 30%. With the
decreasing decomposition rate of mineral matters, the fusion temperature of the sample increases. These account for the fact that AFTs of coal samples increase with the Al2O3 content rising from 10 to 30%.

2.3. Effect of Lower Content of Oxides on AFTs of Coal Samples. 2.3.1. Effect of Na2O on AFTs of Coal Samples. Na2O, content of which is usually lower than 10% in coal ash, plays an important role in the fusibility of coal ash.22 It can be seen from Figure 7 that AFTs of coal samples decrease and then increase with the increase of Na2O content. When the content of Na2O is 9%, the AFT arrives at the minimum. The minimum FT is 1276°C, which is 110°C lower than that of SX coal. It presents that Na2O plays a positive role in the decreasing AFTs.

Figure 7. Effect of Na2O on AFT of coal samples.

Figure 8 demonstrates the coal ash composition with different Na2O contents and the mineral variations for an S/A mole ratio of 2.35 and a CaO/FeO mole ratio of 1.69. The original composition of the SX sample is located in the Ca2SiO4 primary phase field. With the content of Na2O increasing, the chemical compositions of the blended ashes move to the Na2O corner along the straight line. The primary phases of the ashes are mainly CaO. The liquidus temperature decreases and then increases with the increasing Na2O content. When the content of Na2O is 9%, the liquidus temperature of the sample is about 1200°C. However, when the Na2O content is 12%, the liquidus temperature of the sample is about 1600°C. When the Na2O content continues to increase, the liquidus temperature of the sample increases. The trend revealed in the phase diagram is in agreement with the AFT results.

As shown in Figure 9, the first crystalline phases change from MgO to monoxide with different Na2O contents. Moreover, the liquidus temperature decreases from 1800 to 1700°C when the Na2O content increases from 5 to 9%. Then, it increases to 1900°C when the Na2O content is 12%. In addition, the decomposition rate of the mineral varies with different Na2O contents. When the content of Na2O is 5%, the decomposition rate of the mineral is 100/1150%°C. The decomposition rate of the mineral is 100/1000%°C when the content of Na2O is 9%. When the decomposition rate of mineral matters increases, the fusion temperature of the sample decreases. When the content of Na2O increases to 12%, the decomposition rate of the mineral is 100/1350%°C. The above-mentioned reasons may account for the fact that AFTs of coal samples decrease and then increase with the Na2O content increasing.

2.3.2. Effect of K2O on AFTs of Coal Samples. K2O is classified as basic oxide in coal ash,23 the content of which is lower than 10% (wt). Figure 10 shows that AFTs of blended ash samples decrease as K2O content increases, and then increase slightly when the K2O content continues to increase. When the content of K2O is 2%, AFTs of coal samples reach the minimum. The minimum FT is 1317°C, which is 69°C lower than that of SX coal. Furthermore, it can be seen that the DT of blended ash samples is strongly affected by K2O.
Figure 11 illustrates the coal ash composition with different K$_2$O contents and the liquidus temperature for an S/A mole ratio of 2.35. It can be seen from Figure 11 that the liquidus temperature decreases and then increases with the increasing content of K$_2$O. When the content of K$_2$O is 2%, the liquidus temperature of the sample is about 1500 °C. However, when the content of K$_2$O is 6%, the liquidus temperature of the sample is about 1850 °C. When the content of K$_2$O continues to increase, the liquidus temperature of the sample increases. The trend revealed in the phase diagram is similar to the AFT results.

Figure 12 presents the relative mineral mass in the samples with K$_2$O contents of 1, 2, and 4%. It indicates that the liquidus temperature decreases from 1900 to 1700 °C when the content of K$_2$O increases from 1 to 2%. When the content of K$_2$O increases to 4%, the liquidus temperature increases to 1900 °C. In addition, the decomposition rate of mineral matters decreases and then increases with the content of K$_2$O increasing. When the content of K$_2$O is 1%, the decomposition rate of the mineral is 100/1150%/°C. When the content of K$_2$O is 2%, the decomposition rate of the mineral increases to 100/900%/°C. When the content of K$_2$O increases to 4%, the decomposition rate of the mineral decreases to 100/1200%/°C. When the decomposition rate of mineral matters decreases, the fusion temperature of the sample increases. The decomposition rate of mineral variation is the main reason that the AFTs decrease and then increase.

### 2.3.3. Effect of TiO$_2$ on AFTs of Coal Samples.

TiO$_2$ is classified as acid oxide and its content is lower than 2% in coal ash. As shown in Figure 13, AFTs of blended ash samples decrease and then increase with the TiO$_2$ content increasing. When the content of TiO$_2$ is 3% (wt), the AFT reaches the minimum. The minimum FT is 1293 °C, which is 93 °C lower than that of SX coal. It shows that TiO$_2$ plays a positive effect on decreasing AFTs.

Figure 14 represents the coal ash composition with different TiO$_2$ contents and the liquidus temperature for an S/A mole ratio of 2.35 and a CaO/FeO mole ratio of 1.69. The original composition of the SX sample is located in the Ca$_2$SiO$_4$
primary phase field. With the content of TiO$_2$ increasing, the chemical compositions of the blended ashes move to the TiO$_2$ corner along the straight line. The primary phases of ashes are mainly Ca$_5$Ti$_4$O$_{13}$. The liquidus temperature decreases and then increases with the TiO$_2$ content increasing. When the TiO$_2$ content is 3%, the liquidus temperature of the sample is about 1300 °C. When the content of TiO$_2$ is 4%, the liquidus temperature of the sample is about 1400 °C. When the content of TiO$_2$ continues to increase, the liquidus temperature of the blended sample increases. The trend revealed in the phase diagram is consistent with the AFT results.

Figure 15 presents the relative mineral mass with TiO$_2$ contents of 1, 3, and 4%. It is obvious that the liquidus temperature decreases from 1700 to 1600 °C when the TiO$_2$ content increases from 1 to 3%. The liquidus temperature increases to 1800 °C with 4% content of TiO$_2$. When the content of TiO$_2$ is 1%, the decomposition rate of the mineral is 100/100%°C. The decomposition rate of mineral matters increases to 100/800%°C with a TiO$_2$ content of 3%. The decomposition rate of the mineral decreases to 100/1100%°C with a TiO$_2$ content of 4%. With the decreasing decomposition rate of mineral matters, the fusion temperature of the sample increases. The variations of the mineral matter and decomposition rate contribute to the change of AFTs.

2.4. Comparison of the Different Flux. Figure 16 shows that the FT decreases with the flux of Al$_2$O$_3$, TiO$_2$, Na$_2$O, and K$_2$O. The effect of flux on AFTs decreases in the order Na$_2$O > TiO$_2$ > K$_2$O > Al$_2$O$_3$. The best effect is achieved with the Na$_2$O flux and the FT is decreased to 1276 °C. Therefore, the operation temperature of the gasifier can be decreased and oxygen and feedstock could be obviously reduced. Furthermore, refractory life is extended and the cost of industrial production is reduced.

3. CONCLUSIONS
The effects of MgO, Al$_2$O$_3$, Na$_2$O, K$_2$O, and TiO$_2$ on ash fusibility of high-calcium Shanxi coal are studied. Al$_2$O$_3$, TiO$_2$, Na$_2$O, and K$_2$O can decrease the AFTs of coal samples in a certain range. However, the AFTs always increase with increasing MgO content. The DT of the coal sample is strongly affected by K$_2$O. The effect of the flux on AFTs decreases in the order Na$_2$O > TiO$_2$ > K$_2$O > Al$_2$O$_3$.

The phase diagrams depicted by FactSage express the liquidus temperature variation and the change of mineral matters with the composition and temperature. The trend revealed in the phase diagrams and relative mass—temperature curves is consistent with the AFT experiments. The results show that the main reasons for the change of AFTs with different flux are the variation of mineral matter and decomposition rate.

4. EXPERIMENTAL SECTION
4.1. Coal Sample. A representative high-calcium coal, Shanxi coal (denoted as SX coal), is selected in this work.
Proximate analysis and ultimate analysis of SX coal are listed in Table 1. According to the Chinese standard GB/T212-2008, the ash samples are prepared in a muffle furnace at 815 °C. The chemical compositions of SX coal ash are given in Table 2.

### Table 1. Proximate Analysis and Ultimate Analysis of SX Coal

| sample | M_d | A_d | V_d | FC_d | C_d | ultimate analysis, daf wt % |
|--------|-----|-----|-----|------|-----|-----------------------------|
| Shaxi  | 15.21 | 2.77 | 28.87 | 53.15 | 78.65 | H_d | O_d | N_d | S_d |
|        |      |      |      |      |      | 4.13 | 12.94 | 0.95 | 0.06 |

Note: ad: air dry; daf: 1:by difference; 2: total sulfur.

### Table 2. Ash Chemical Composition of SX Coal

| ash sample | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | Na_2O | K_2O | TiO_2 | SO_3 | TiF_2 | Ash chemical compositions wt % | AFTs/C |
|------------|-------|---------|---------|-----|-----|-------|------|-------|------|-------|-----------------------------|--------|
| Shaxi      | 10.91 | 7.88    | 26.55   | 31.49 | 10.12 | 0.41 | 0.24 | 11.54 | 0.42 | 0.40 | DT | 1288 | 1291 | 1305 | 1386 |

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