Influence of Ashing Temperature on Predicting Slagging Characteristics of Xinjiang High-Sodium Low-Rank Coal and Strategy of Using Mineral Additives as Potential Slagging Preventatives

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ABSTRACT: It is crucial to accurately evaluate the slagging characteristics of coal before industrial application. However, when evaluating the Xinjiang high-sodium low-rank coal (XJc) according to the properties of the ash prepared at 815 °C, the ashing temperature of the coal sample specified by Chinese standards, forecasting failures are frequent. To figure out the internal reason, the influence of ashing temperature on predicting slagging characteristics of XJc was investigated via an ashing test and thermodynamic equilibrium calculation. Experimental results show that when XJc is ashed at 815 °C, the ash yield apparently reduces compared to the case when ashed at 500 °C since numerous volatile components are released. The release of these components contributes to an obvious inhibition in the formation of the liquid phase in the residual ash, especially at temperatures below 1200 °C. Hence, reducing the ashing temperature is conducive to the acquirement of more real ash compositions of XJc and thereby to the accurate prediction of the slagging behaviors. By a comparison with reported experimental results, it is found that the liquid ratio–temperature curve calculated from the ash compositions of the ash prepared at 500 °C basically reflects the actual slagging tendency of XJc. According to the evolution of minerals with temperature, two slagging mechanisms, self-fusion of sodium-bearing salts and low-temperature eutectics, are confirmed. In addition, effects of antislagging measures of adding refractory oxides greatly differ among coal types due to the diversity in ash compositions.

1. INTRODUCTION

Slagging is a major issue limiting coal utilization. With the exploitation and utilization of Xinjiang high-sodium low-rank coal (XJc) in Northwest China, the slagging issue has become more prominent in recent years.1,2 Due to the lack of adequate knowledge on this type of coal and an effective prediction of slagging, most XJc-firing boiler plants suffer from a severe slagging problem at an early stage, resulting in frequent safety incidents and unscheduled shutdown of boiler units. Research has shown that a high content of alkali and alkaline earth metals (AAEMs) in the coal ash was responsible for this issue.3–5

For an early warning, accurately predicting slagging characteristics of coal before industrial application is necessary. Most current predictions are based on ash fusibility and ash compositions. Regarding the determination of ash fusibility, the most common approach is to measure the ash fusion temperatures (AFTs) via the ash cone fusion test, including the deformation temperature (DT), the softening temperature (ST), the hemispherical temperature (HT), and the fluid temperature (FT). AFTs reflect the real melting state of coal...
ash; thus, the prediction based on AFTs is relatively accurate in theory. To date, numerous correlative indices have been proposed to evaluate the slagging tendency of coal.\(^8\) According to the concept of ionic potential, ash compositions are classified into acidic oxides (SiO\(_2\), Al\(_2\)O\(_3\), and TiO\(_2\)) and alkaline oxides (Na\(_2\)O, K\(_2\)O, MgO, and CaO).\(^9\) The former generally increase AFTs, whereas the latter decrease AFTs.

Following such relevance, many slagging indices have also been proposed to predict the slagging characteristics of coal.\(^6\) However, in some cases, impacts of certain important components such as sulfur\(^10\) and chlorine are frequently ignored.

When evaluating the slagging characteristics of XJc using the above-mentioned methods, the accuracy is often questionable. For instance, Zhou et al.\(^11\) pointed out that the measured AFTs via the ash cone fusion test were too high to accurately evaluate the actual slagging situations of industrial XJc-firing boilers. In much of the reported literature,\(^12,13\) there was also a mismatch between measured ash compositions and actual slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics. The poor prediction most likely resulted from the enrichment of highly volatile AAEMs in slagging characteristics.

For XJc, the ash yield at 815 °C almost halved, compared to the case at 400 °C.\(^15\) Further analysis showed that the release of sodium, sulfur, and chlorine was significantly responsible for the huge ash loss. In actual combustion and gasification conditions, the species released are probably recaptured by ash particles under the action of gas-solid disturbance, promoting the slagging.\(^9,16,17\) However, in the static ashing process and the ash cone fusion test, this cannot be achieved. This viewpoint is supported by a reported result that the ST of XJc ash prepared at 500 °C was about 100 °C lower than that prepared at 815 °C.\(^19\) In the studies of Li et al.\(^20\) and Yao et al.,\(^21\) similar results were also reported. Besides the inaccuracy of prediction, large discrepancies in properties of XJc among different mines\(^22\) also increase the difficulty in understanding the slagging mechanisms\(^23\) and reduce the universality of an antislagging method.

To date, thermodynamic equilibrium calculation has been widely used to evaluate the slagging characteristics of coals.\(^24,25\) For XJc, due to the aforementioned impacts of ashing temperature, the accuracy of thermodynamic equilibrium calculation based on the ash prepared at a certain ashing temperature may be questionable. To the best of the authors’ knowledge, the influence of ashing temperature on the accuracy of such a calculation has not been determined.

Against this research gap, the variation of ash compositions of XJc with ashing temperature was first investigated in this study. Then, the impact of ashing temperature on the calculating accuracy was evaluated by a comparison with the reported experimental results. After that, the detailed slagging characteristics of XJc and antislagging strategies via adding mineral additives were discussed by a thermodynamic equilibrium calculation. Considering the diverse properties of XJc mined from different coalfields, four kinds of XJc were used. Two kinds of non-XJc were also studied for comparison.

### 2. FUEL AND METHOD

#### 2.1. Fuel

Four kinds of XJc (TMc, TWc, SHc, and SEc) and two kinds of non-XJc (SMc and DTc) were used. The six kinds of coal were characterized to obtain the results of proximate and ultimate analyses, ash compositions, and ash fusibility, according to Chinese standards including GB/T 212-2008, GB/T 476-2001, GB/T 1574-2007, and GB/T 219-2008. As required by these standards, the coals were ashed at 815 °C. The analysis results of coal are given in Table 1.

### Table 1. Properties of Coal Used in This Study

| coal     | TMc | TWc | SHc | SEc | SMc | DTc |
|----------|-----|-----|-----|-----|-----|-----|
| proximate analysis (wt %, air-dry basis) |     |     |     |     |     |     |
| fixed carbon | 55.48 | 49.94 | 45.27 | 43.86 | 55.03 | 47.13 |
| volatile | 27.02 | 26.12 | 34.06 | 30.46 | 32.51 | 29.75 |
| ash | 3.16 | 9.88 | 5.03 | 14.66 | 4.76 | 18.39 |
| water | 14.34 | 14.06 | 15.64 | 11.02 | 7.70 | 4.73 |
| LHV (MJ/kg) | 23.70 | 21.84 | 17.63 | 17.93 | 27.68 | 23.72 |

| ultimate analysis (wt %, air-dry basis) |     |     |     |     |     |     |
| ash compositions (wt %) |     |     |     |     |     |     |
| SiO\(_2\) | 3.73 | 20.81 | 17.24 | 41.98 | 28.40 | 49.54 |
| Al\(_2\)O\(_3\) | 6.16 | 10.54 | 11.90 | 17.59 | 12.95 | 34.88 |
| Fe\(_2\)O\(_3\) | 5.37 | 29.70 | 5.76 | 6.78 | 10.62 | 4.34 |
| CaO | 33.45 | 11.36 | 28.74 | 19.39 | 30.60 | 5.64 |
| MgO | 5.42 | 4.51 | 5.34 | 2.49 | 1.05 | 0.38 |
| TiO\(_2\) | 0.41 | 0.60 | 0.60 | 0.98 | 0.57 | 0.50 |
| SO\(_3\) | 29.34 | 14.91 | 19.58 | 1.82 | 10.66 | 2.78 |
| P\(_2\)O\(_5\) | 0.00 | 0.04 | 0.05 | 0.18 | 0.20 | 0.00 |
| K\(_2\)O | 0.45 | 0.89 | 0.38 | 0.66 | 0.42 | 0.31 |
| Na\(_2\)O | 7.28 | 2.71 | 3.92 | 4.38 | 1.40 | 0.10 |
| others | 8.39 | 3.93 | 6.49 | 3.75 | 3.13 | 0.61 |
| ash fusion temperatures (AFTs, °C) |     |     |     |     |     |     |
| DT | 1360 | 1110 | 1320 | 1120 | 1200 | 1270 |
| ST | 1370 | 1130 | 1320 | 1130 | 1210 | 1470 |
| HT | 1370 | 1150 | 1330 | 1140 | 1220 | >1500 |
| FT | 1380 | 1170 | 1340 | 1150 | 1240 | >1500 |

*LHV, low heating value.*

Results show that all four kinds of XJc’s are rich in AAEMs. Even so, the measured AFTs of TMc and SHc fail to accurately reflect their actual slagging behaviors. Similar to XJc, SMc is also a low-rank coal but contains less alkali metals. During the early use, SMc had demonstrated a certain slagging tendency,\(^26,27\) while DTc is widely considered to be free from ash-related problems.

### 2.2. Ashing Test and Sample Characterization

The ashing test was conducted at 500—1000 °C, at a temperature interval of 100 °C. Each coal sample underwent a slow heating process. For instance, the temperature program in the case of 800 °C was as follows. In the air, the coal sample was first heated from room temperature to 400 °C within 1 h and the temperature of 400 °C lasted for 2 h; then, the temperature was raised to 600 °C within 1 h and the ashing process was kept at 600 °C for 1 h; after that, the temperature continued to be raised to 800 °C within 1 h and the residual was further ashed for 4 h.
Ash samples were characterized using an X-ray fluorescence spectrometer (XRF, XRF-1800, Japan) and an X-ray diffractometer (XRD, Panalytical, The Netherlands) to determine the ash compositions and crystalline phases, respectively.

2.3. Thermodynamic Equilibrium Calculation. In this study, the software of Factsage 7.2 was employed. Since the ashing process of 500 °C sufficiently burned the coal out and effectively reduced the escape of alkali metals,28 the data of ash compositions of the coal ashed at 500 °C were input for calculations. The databases of FactPS, FToxid, FTsalt, and FTmisc were selected, as well as the product species of ideal gas, pure liquids, pure solids, and corresponding solution phases. The calculation was conducted at 600–1500 °C with an interval of 25 °C, at 0.1 MPa. Although the reaction atmosphere plays an important role,10 the calculation was carried out in an inert atmosphere according to ref24. Via the calculation, the evolution of the mineral phase in the ash prepared at temperatures of 500 and 800 °C was compared, and the influence of ash composition was evaluated.

3. RESULTS AND DISCUSSION

3.1. Influence of Ashing Temperature on the Release of Ash. Figure 1 shows the ash yield of experimental coal as a function of ashing temperature. For the four kinds of XJc, the experimental ash yields gradually reduce as the ashing temperature increases. The apparent downward trend indicates that the ashes are highly reactive and unsteady, even at the temperature below 815 °C. However, for non-XJc, the changes in ash yield are significant only in the narrow temperature range of 600–700 °C and very limited in the range of 700–1000 °C. When the temperature exceeds 1000 °C, the ash yields recover the apparent downward trend. A similar trend was also observed in the study of Yao et al.29 They considered that the weight loss was assigned to the oxidation of unburned and encapsulated char because at such high temperatures the melting of ash allowed oxygen diffusion. However, in this study, the huge weight loss is only attributed to the ash escape. It should be noted that even at a temperature as high as 1200 °C, the ash yield of DTc is still up to 93%, indicating that DTc ash is thermally inert. Hence, mechanisms of ash loss are highly different between XJc and non-XJc.

Figure 2 shows the ash composition of coal ash by XRF as a function of ashing temperature. According to the variations of content of ash composition with temperature, the thermal behaviors of calcium, sodium, sulfur, and chlorine in the ashing process shall be focused to reveal the ash loss mechanisms. As indicated by XRD patterns in Figure 3, these species mainly exist in the raw coal (referring to the coal ash prepared at 500 °C) in forms of anhydrite (CaSO₄), calcite (CaCO₃), halite (NaCl), and sodium sulfate (Na₂SO₄). As the ashing temperature increases from 500 to 700 °C, the diffraction peak of calcite gradually disappears, which is extremely consistent with the decomposition feature of calcite.² It is inferred that the decomposition of calcite chiefly contributes to the ash loss of experimental coals excluding TWc at the corresponding temperature range. For XJc, with an increase in ashing temperature, the lime (CaO) decomposed from calcite rapidly reacts with other minerals, forming gehlenite (Ca₂Al₂SiO₇), diopside (Ca₂MgSi₂O₆), etc. However, for non-XJc, such an evolution of lime seems not to occur or to be very weak since the apparent peak of lime still exists.

Figure 2 clearly shows that contents of both sodium and chlorine gradually decrease with temperature for TMc, SHc, and SEc. At 900 °C, there was almost no chlorine in ash. To date, the occurrence modes and transformation behaviors of sodium and chlorine in the low-rank coal have always been of concern. In the coexistence of sodium and chlorine, the two elements may exist and release in the form of NaCl.15 XRD
patterns in Figure 3d strongly confirm such a behavior of sodium and chlorine in SEc.

Figure 4 shows the molar ratio of Na/Cl released on the basis of the ash prepared at 500 °C. For facilitating analysis, molar ratios of Na/Cl presented in the ash prepared at 500 °C are also presented. It is found that both molar ratios of Na/Cl exceed the value of 1. In theory, if there exist more sodium and chlorine in the form of NaCl, the ratio will be closer to 1. For the three coals presented in Figure 4, the deviation of the ratio away from 1 basically follows the descending order of TMc, SHc, and SEc. According to the deviation, it is inferred that for TMc and SHc there may still be a considerable amount of sodium and chlorine existing in other forms besides NaCl, while for SEc, most of the sodium and chlorine may be present in the form of NaCl. The observation of cubic-shaped NaCl crystal particles on the ash deposition probe verified that the two elements migrated in the form of NaCl.30 Figure 4 can be explained by our previous findings23 that the content of NH4Ac-soluble sodium in XJc follows the descending order of TMc (36.2%), SHc (12.4%), and SEc (7.9%). The NH4Ac-soluble sodium in coal exists as ion-exchangeable cations associated with the carboxyl groups, forming part of the organic coal substance.31 At high temperatures, such sodium will be transformed into atoms,32 oxides, and carbonates17 and subsequently released into the gas, resulting in the ratio released away from the value of 1.

At the temperature above 700 °C, the peak of sodium disilicate (Na2Si2O5) emerges, as shown in Figure 3a,c. It indicates that sodium disilicate is easily formed. Actually, sodium disilicate can be generated via the reaction between silica (SiO2) and NaCl in the presence of moisture,17 releasing gaseous chlorine in the form of HCl. However, in such an ashing process, moisture is absent, and thus this reaction is impossible. A possible reaction generating sodium disilicate is the one between silica and Na2SO4.3 Sodium disilicate and sodium sulfate have a low melting point, 874 and 884 °C,

Figure 3. XRD patterns of experimental coal ashes at different ashing temperatures: (a) TMc, (b) TWc, (c) SHc, (d) SEc, (e) SMc, and (f) DTc. A, anhydrite_\text{CaSO}_4; Ss, sodium sulfate_\text{Na}_2\text{SO}_4; Sd, sodium disilicate_\text{Na}_2\text{Si}_2\text{O}_5; C, calcite_\text{CaCO}_3; L, lime_\text{CaO}; He, hemalite_\text{Fe}_2\text{O}_3; Q, quartz_\text{SiO}_2; D, diopsid\text{e}_\text{Ca}_2\text{MgSi}_2\text{O}_6; G, gehlenite_\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7; Ha, halite_\text{NaCl}; M, merwinite_\text{Ca}_2\text{Mg}(\text{SiO}_4)_2.
respectively. These low-melting-point components make XJc face a potential risk of slagging.

Different from TMc, SHc, and SEc, the ash loss of TWc is apparently caused by the decrease of sulfur rather than sodium and chlorine. Figure 2b shows that as the temperature increases from 500 to 1000 °C, the content of SO3 reduces by almost 74%. Thus, the sulfur in TWc is thermally unsteady. Such sulfur-bearing components include sulfides, sulfur, organic sulfur, etc. However, these components are not detected by XRD analysis in this study.

The above results imply that when the ashing temperature of 815 °C is employed, for XJc, a lot of ash, mainly composed of sodium, chlorine, sulfur, and calcium, escapes. Hence, the test results based on the ash prepared at 815 °C cannot truly characterize the XJc. There is of course a certain gap between the prediction of slagging using these data and the actual situation. However, during the calculation, all phases are kept in an equilibrium state under the principle of minimum Gibbs free energy, i.e., the interaction among minerals is adequate. As shown in Figure 1, the calculated ash yields are apparently higher than the experimental ones and basically remain constant at temperatures below 1000 °C. This confirms that during the calculation the low-temperature release of minerals is considerably relieved, which is a prerequisite for subsequent evaluation of slagging characteristics using the calculating results. More detailed discussions will be made later.

### 3.2. Slagging Characteristics Based on the Liquid Ratio

Here, we compared two cases of ashing temperatures of 500 and 800 °C to illustrate the influence of ashing temperature. The liquid ratio, which is defined as the mass percentage of the liquid phase (including liquid slags and liquid pure compounds) in the residual slags, is adopted to evaluate the slagging characteristics. The relevant results calculated via FactSage 7.1 are shown in Figure 5.

As illustrated in Figure 5, the liquid ratio in the case of 500 °C is basically higher than that in the case of 800 °C, especially for XJc. Hence, when a higher ashing temperature is used, the predicting slagging characteristics of XJc will be less severe than the actual situations. The differences between the two liquid ratio–temperature curves reflect the importance of released species to slagging. For the cases of XJc, the two curves significantly differ, but for the cases of non-XJc, the trends of the two curves are very similar. According to this point, it is believed that the released species play an important role in promoting slagging for XJc but not for non-XJc. Through further observation, it is found that for XJc the main differences between the two curves (500 and 800 °C) exist in the temperature ranges of 800–1350 °C (TMc), 900–1150 °C (TWc), 1000–1450 °C (SHc), and 800–1275 °C (SEc).

Therefore, when using ash compositions of the ash prepared at 815 °C, a lot of information important to understand the low-temperature slagging mechanism of XJc will be missed. In other words, the calculating results based on the ash preparation method specified by Chinese standards are questionable before further confirmation.

It is also seen in Figure 5 that the diversity between the cases of 500 and 800 °C varies considerably among the four kinds of XJc’s. This may be explained by the differences in the amount and species of ash composition released. For instance, for the case of TWc, a small difference corresponds to a low ash loss
(see Figure 1). The detailed influence of ash composition released will be discussed in Section 3.3.

Slagging characteristics of XJc will next be analyzed based on the liquid ratio–temperature curves of the case of 500 °C. According to the curves, it is found that the liquid ratio of TMc rapidly increases to about 50% at 900 °C. For TWc, the starting temperature with a rapid growth in liquid phases is 1100 °C. Within a temperature increase of only 50 °C, the liquid ratio increases by almost 43%, from 7.2 to 51.2%. For SHc, the temperature range corresponding to a fast increase in the liquid phase is 900–1000 °C. In this temperature range, the ratio increases from 4 to 31%. Unlike the other three kinds of XJc’s, SEc is not characterized by a low-temperature zone with a fast increase in the liquid ratio. However, at a temperature as low as 800 °C, the liquid phase remains at a high level, accounting for up to 18%, and gradually increases until a steep rise at 1275 °C. Based on these results mentioned above, it is predicted that all four kinds of XJc’s are characterized by severe low-temperature slagging characteristics.

To verify the rationality of aforementioned predictions, the liquid ratio–temperature curves are further analyzed combining the experimental results of TMc and SHc. Figure 6a shows the variation of bed temperature with time during circulating fluidized-bed gasification (CFBG) of TMc. During the process of CFBG, the melting substances will adhere to the surface of the bed material or ash particles, resulting in a phenomenon of slagging, named agglomeration. In this study, agglomeration is considered as a phenomenon of slagging. To better explain our calculating results, agglomeration is assumed to mainly result from the release of certain ash compositions is the main reason for the differences in slagging characteristics between the cases of 500 and 800 °C. For TMc, SHc, and SEc, the ash released primarily includes Na2O, CaO, and Cl, while for TWc, SO3 contributes to the ash loss. To reveal the separate effect of each volatile ash composition on slagging characteristics, the liquid ratio–temperature curves as a function of their contents are calculated, as shown in Figure 7. Note that the effect of CaO will be discussed as a mineral additive in Section 3.5; thus, the result of CaO is not presented in Figure 7.

3.3. Influence of Release of Ash on the Liquid Ratio.

As mentioned above, the release of certain ash compositions is the main reason for the differences in slagging characteristics between the cases of 500 and 800 °C. For TMc, SHc, and SEc, the ash released primarily includes Na2O, CaO, and Cl, while for TWc, SO3 contributes to the ash loss. To reveal the separate effect of each volatile ash composition on slagging characteristics, the liquid ratio–temperature curves as a function of their contents are calculated, as shown in Figure 7. Note that the effect of CaO will be discussed as a mineral additive in Section 3.5; thus, the result of CaO is not presented in Figure 7.

It is clearly seen from Figure 7a,d that as the content of Na2O increases, for TMc and SHc, the liquid ratio is on the rise. By further comparing the two black lines outlined on the surface, the rising trend is relatively apparent at temperatures above about 900 °C. Such an influence of Na2O matches the results shown in Figure 5a,c, indicating the important role of sodium in promoting slagging.

By contrast, for SEc, the influence of Na2O is worth attention. The biggest difference to cases of TMc and SHc is that when the Na2O content decreases, the liquid ratio increases at low temperatures below 800 °C; see Figure 7f. This special trend may be attributed to the special coal property of SEc, the feature of a high content of chlorine. In the two cases of 500 and 800 °C, the molar ratios of Na/Cl in
the ash are 1.35 and 0.41, respectively. According to the two ratios, chlorine is considered to be more inclined to exist in the form of NaCl in the case of 500 °C and in the form of other metal chlorides, such as CaCl₂, MgCl₂, etc., in the case of 800 °C. It is known that the melting points of alkaline earth metal chlorides are generally lower than that of NaCl (801 °C). For instance, the melting points of CaCl₂ and MgCl₂ are 772 and 714 °C, respectively, and FeCl₂ melts at 670–674 °C. Hence, when the Na₂O content in SEc decreases, there will be more alkaline earth metal chlorides. The lower-temperature melting of metal chlorides is responsible for the higher liquid ratio at a low temperature.

For TWc, the decrease in the SO₃ content results in a decrease in the liquid ratio, as indicated by Figure 7c. The input content of other ash compositions has been normalized based on the corresponding content in the ash prepared at 500 °C.

Figure 7. Three-dimensional color mapping surfaces of the liquid ratio for Xjc, for which independent variables are the temperature and content of volatile ash composition: (a) Na₂O_TMc, (b) Cl_TMc, (c) SO₂_TWc, (d) Na₂O_SHc, (e) Cl_SHc, (f) Na₂O_SEc, and (g) Cl_SEc. The two black lines outlined on the surface indicate the two liquid ratio—temperature curves of the ash in which the content of ash composition is equal to the corresponding value in the ash prepared at 500 and 800 °C, respectively.
decreasing trend of the liquid ratio mainly exists at 900–1100 °C, coinciding with the results of Figure 5b. In Figure 7b,e,g, it is seen that the liquid ratio increases overall with the decreasing content of chlorine, especially at temperatures above 900 °C. Generally, chlorides have strong volatility. As the content of chlorine increases, more alkali and alkaline earth metals, important fluxing materials, prefer to be released into the gas phase in the form of chlorides. Results of Figure 8 that more gaseous species are released with an increase in both temperature and content of chlorine confirm this view. However, such an influence of chlorine is contrary to that of Na₂O and SO₃.

Besides, as indicated by Figure 5, with an increase in ashing temperature (namely, with a decrease in the chlorine content), the liquid ratio overall decreases. There is a contradiction between Figures 7 and 5. It is because the influence of a single component is one-sided and the final slagging characteristics are the integrated result of all components in the ash.

3.4. Evolution of Mineral Phase with Temperature. Figure 9 shows the phase assemblage—temperature curves for XJC, which are calculated using the ash compositions of the ash prepared at 500 °C as input data. The input ash compositions will be converted into corresponding solid, liquid, and gas phases, following the principle of minimum Gibbs free energy. According to the evolution of phase assemblage, the detailed slagging mechanisms of XJC can be revealed.

As shown in Figure 9a, it is inferred that the low-temperature slagging mechanism of TMc includes two parts, fast growth of liquid slags at 800–825 °C and melting of Na₂SO₄ at 884 °C. According to the evolution of minerals, the liquid slags (the phase of SLAG presented in Figure 9) mainly originate from low-temperature eutectics, composed of...
Figure 10. Three-dimensional color mapping surfaces of the liquid ratio for XJC, for which independent variables are temperature and content of refractory oxide: (a.1) CaO_TMc, (a.2) Al₂O₃_TMc, (a.3) SiO₂_TMc, (b.1) CaO_TWc, (b.2) Al₂O₃_TWc, (b.3) SiO₂_TWc, (c.1) CaO_SHc, (c.2) Al₂O₃_SHc, (c.3) SiO₂_SHc, (d.1) CaO_SEc, (d.2) Al₂O₃_SEc, and (d.3) SiO₂_SEc. The black line outlined on the surface indicates the liquid ratio—temperature curve of the ash prepared at 500 °C.
The mechanism of SHc is also divided into two parts, the self-melting and the second fast growth of liquid slags. The self-melting of Na2SO4 at 884°C contributes to the high liquid ratio at above 97%. The molar ratio of O/S is 3.01, indicating that Na2SO4 initiates the whole low-temperature slagging process. TWc, agreeing with the variation of content of SO3 in ash with temperature. For TWc Na2SO4 also plays an important role in promoting slagging. The self-melting of Na2SO4 is inferred to be responsible for the high liquid ratio at above 1100°C. The main components in the liquid slags consist of SiO2 (36.3%), Al2O3 (19.6%), CaO (10.9%), Na2O (8.1%), MgO (7.4%), CaSO4 (6.0%), MgSO4 (5.0%), Na2SO4 (4.2%), etc. Overall, Na2SO4 initiates the whole low-temperature slagging process. The mass fraction of GAS begins to rise at above 1000°C. At above 900°C, the GAS accounts for 23.7%. Actually, the GAS mainly consists of two elements, oxygen and sulfur, accounting for above 97%. The molar ratio of O/S is 3.01, indicating that the GAS may originate from the decomposition of sulfates and the two elements most likely exist in the form of SO3. Al2O3 and CaO are generally refractory oxides, not conducive to slagging. However, under the action of alkali metal components such as NaCl, Na2O, and Na2SO4, these refractory oxides are dissolved. The second fast growth of liquid slags occurs at above 1400°C, and the fluxing materials chiefly originate from CaSO4, Ca3SiO5, etc. Meanwhile, the mass fraction of the GAS (the gaseous species released from residual slags) starts to evidently increase. The released components primarily contain chlorine, sodium, oxide, sulfur, and potassium, which are commonly considered as crucial components causing the fouling.

It is seen from Figure 9b that for TWc Na2SO4 also plays an important role in promoting slagging. The self-melting of Na2SO4 is inferred to be responsible for the high liquid ratio at above 900–1000°C as presented in Figure 5b. After that, the molten Na2SO4 may react with Mg2SiO4, generating Mg2SiO4 and NaAlSiO4. NaAlSiO4 has a melting point of 1100°C. At above 1100°C, the molten NaAlSiO4 gradually dissolves other solid minerals including CaSO4, Mg2SiO4, and residual MgAl2SiO5. At this moment, the liquid slags start to form fast. At 1100–1200°C, the liquid content increases from about 0 to 48.6%. The calculating results show that at 1200°C, the main components in the liquid slags consist of SiO2 (36.3%), Al2O3 (19.6%), CaO (10.9%), Na2O (8.1%), MgO (7.4%), CaSO4 (6.0%), Mg2SiO4 (5.0%), Na2SO4 (4.2%), etc. Overall, Na2SO4 initiates the whole low-temperature slagging process. The mass fraction of GAS begins to rise at above 1000°C. At 1500°C, the GAS accounts for 23.7%. Actually, the GAS mainly consists of two elements, oxygen and sulfur, accounting for above 97%. The molar ratio of O/S is 3.01, indicating that the GAS may originate from the decomposition of sulfates and the two elements most likely exist in the form of SO3. The calculating results confirm the strong volatility of sulfur in TWc, agreeing with the variation of content of SO3 in ash with ashing temperature shown in Figure 2b.

As indicated by Figure 9c, the low-temperature slagging mechanism of SHc is also divided into two parts, the self-melting of Na2SO4 at 884°C and the generation of liquid slags at above 1000°C. Such a slagging mechanism is similar to that of TMc. According to the evolution of phases, the rapid growth of liquid slags from 3.8 to 17.7% at ~1000°C mainly results from the interaction of Na2Ca3Al16O28-Ca2Fe2O5-Fe2O3, etc. As the temperature further increases, Na2Ca3Al16O28, Ca2MgSi2O6, Ca2Al2SiO7, and CaSO4 successively dissolve, further promoting the growth of liquid slags. At 1375–1500°C, the mass fraction of GAS gradually increases to 12.6%. In the GAS, the main elements include oxide, sulfur, chlorine, and sodium. Despite the content of iron being relatively high in TWc (see Table 1), the iron oxide always exists in the form of Fe2O3, even at high temperatures, which is consistent with the XRD patterns in Figure 3b and other reported results.

Due to the high content of NaCl, the slagging characteristics of SEc are certainly different from those of the other three kinds of XJc. As shown in Figure 9d, NaCl contributes to the first fast growth of liquid slags at below 800°C. In the liquid slags, the mass fraction of molten NaCl accounts for 88.6%. In the temperature range of 925–950°C, mass percentages of NaAlSiO4 and Ca2Al2SiO7 start to increase. The two phases may be generated by reactions between Ca2Fe2Si2O10 and Na2Ca2Al16O28. Although NaAlSiO4 and Ca2Al2SiO7 have high melting points, 1520 and 1593°C, respectively, they are dissolved into the liquid slags at 1275–1300°C, thereby increasing the liquid slags from 26.2 to 94.9%. This is a typical low-temperature eutectic phenomenon of XJc. In addition, numerous components in SEc start to release at ~1300°C. At 1500°C, the mass fraction of GAS is up to 23.1%. Obviously, the gaseous NaCl is dominant in the GAS, accounting for a volume fraction of 55.1%. Other gas components mainly include SO3 (NaCl2), KCl, etc.

### 3.5. Influence of Refractory Oxide on Antislagging

Refractory oxides in coal usually play a role in improving resistance to ash fusibility, which provides a guide to solving the ash-related problems during coal thermal conversion by blending coal or adding mineral additives. In this study, the liquid ratios at varying temperatures and varying contents of CaO, Al2O3, and SiO2 are calculated. Relevant results are shown in Figure 10.

Figure 10a.1–a.3 shows the 3D color mapping surfaces of liquid ratios in TMc ash. By a comparison with the ash prepared at 500°C, it is found that varying the contents of all three oxides in TMc can regulate the slagging characteristics of TMc. For instance, the decreasing trend of liquid ratio with the increasing content of CaO indicates that adding CaO (i.e., the content of CaO exceeds 32.8%) improves the resistance to ash fusibility. The improving effect is significant, especially at above 900°C. Besides the high melting point (2572°C) of CaO, the improvement can also be achieved by prior reactions of CaO with other coal ash (such as SiO2 and Al2O3) inhibiting the generation of sodium-based eutectics.41 However, different situations occur for the cases of Al2O3 and SiO2. As seen in Figure 10a.2, the proportion of the liquid phase in ash effectively reduces at temperatures above 800°C only when the content of Al2O3 exceeds ~20%. Otherwise, the liquid ratio increases. The low content of Al2O3 in the ash of TMc (only 4.7%; see Figure 2a) may be responsible for the increasing liquid ratio. According to the variation of the liquid ratio, Al2O3 plays a role of a fluxing material within the content range of 8–20%. As indicated by Figure 10a.3, at contents below ~14%, SiO2 also performs a fluxing function. It has been reported that the low-content addition of silicon- and aluminum-bearing additives in the Xinjiang high-sodium coal lowers the ash fusion temperatures.42 For TMc, SiO2 performs the best antifluxing behavior at the content of ~20%. Under this circumstance, SiO2 may prefer to react with other ash compositions, forming higher-melting-point components. However, at other contents of SiO2 (~55%), the liquid ratio basically remains at a high level, regardless of the content. It indicates that the antislagging measure by adding SiO2 is invalid in most cases.

As observed in Figure 10b.1, for TWc, largely increasing the content of CaO is invalid. When the content of CaO is higher than 27%, the ash fusibility is significantly improved. It is quite contrary to the case of TMc. Figure 10b.2 shows that in the temperature range of 900–1275°C a higher content of Al2O3 in TWc basically corresponds to a lower liquid ratio. In this circumstance, the participation of Al2O3 contributes to the mitigation of slagging. An increase in SiO2 is only conducing to the reduction of generating a liquid phase at 900–1000°C, as
indicated by Figure 10b.3. At a higher temperature above 1100 °C, however, adding SiO₂ results in more liquid phases.

It is found that there are similarities in variation trends of 3D color mapping surfaces between TMc and SHe, by comparing Figure 10a.1—a.3 and c.1—c.3. However, effects of adding refractory oxides in antislagging are discrepant due to different contents of ash compositions in the two ashes. As observed in Figure 10c.1, increasing the CaO content from 29 to 41% largely accelerates the generation of the liquid phase, especially at temperatures below 1300 °C. After that, although increasing the CaO content results in a reducing liquid ratio, the liquid ratio still remains at a high level. This indicates that CaO plays a role of fluxing in the SHe case. Because of an insignificant growth of the liquid phase, adding Al₂O₃ or SiO₂ does not cause severe slagging risk. This trend is different from the low-temperature fluxing action of Al₂O₃ and SiO₂ in the TMc case. Similar to the case of TMc, however, the lowest liquid ratio also appears at the SiO₂ content of ~20%.

Adding CaO into SEc is also unfavorable to inhibit the formation of a liquid phase, as indicated by Figure 10d.1, because the participation of CaO promotes the formation of low-temperature eutectics. Figure 10d.2 and d.3 indicates that Al₂O₃ can be used as a mineral additive for antislagging, whereas adding SiO₂ cannot achieve this purpose.

4. CONCLUSIONS

In the temperature range of 500–1200 °C, the yield of coal ash decreases with an increase in the ashing temperature. The weight loss of coal ash is mainly attributed to two parts, the decomposition of calcite at 600–700 °C and the release of volatile components including calcium, sodium, sulfur, chloride, etc. The former is largely responsible for the ash loss of high-rank coal such as DTC, whereas the latter mainly results in the ash loss of low-rank coal such as XJc and SMC. Compared to the case of 500 °C, at the ashing temperature of 815 °C, numerous volatile components in XJc ash are released. Thermodynamic equilibrium calculation shows that these released components play an important role in promoting the formation of the liquid phase, especially at temperatures below 1200 °C. This may be a main reason for the inaccurate prediction of slagging characteristics of XJc using the ash compositions of the ash prepared at 815 °C. However, for non-XJc (SMc and DTC), such an adverse influence caused by a higher ashing temperature is basically negligible, regardless of the coal rank. By a comparison with reported experimental results, it is found that the liquid ratio—temperature curve calculated from the ash compositions of the ash prepared at 500 °C can reflect the actual slagging characteristics of XJc. According to the curves, all four kinds of XJc’s are predicted to suffer from a low-temperature slagging issue. This issue mainly results from the self-fusion of sodium-bearing salts and the low-temperature eutectics. The antislagging measures of adding refractory oxides greatly differ among the four kinds of XJc’s due to the diversity of ash compositions. In most cases, adding SiO₂ (the content of SiO₂ is below 60%) seems invalid for antislagging, while the addition of Al₂O₃ into XJc performs an excellent antislagging function. In addition, adding CaO to inhibit the slagging issue seems effective only for TMc.

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Notes
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