Research on the Ash Melting Characteristics of Blended Coal Based on DFT Calculations

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ABSTRACT: Low-ash-melting-point bituminous coal and high-ash-melting-point anthracite coal are mixed and burned in different proportions. The ash melting characteristics of blended coal were determined experimentally. At the same time, the ash samples of bituminous coal, anthracite, and blended coal were analyzed by X-ray diffraction (XRD), and the ash melting characteristic improvement mechanism of blended coal was analyzed by quantum chemical calculations. The results show that when high-ash-melting-point anthracite is added, the ash melting characteristics of blended coal are improved, and the deformation temperature, softening temperature, hemispheric temperature, and flow temperature of the blended coal are significantly increased. The melting point of blended coal ash with a bituminous coal ratio of less than 50% can meet the requirements of blast furnace injection. The reason for the improved melting characteristics of the blended coal ash is that mullite in anthracite ash reacts with gehlenite in bituminous coal ash during the combustion process to produce anorthite.

1. INTRODUCTION

Energy security is an overall and strategic issue related to national economic and social development, which is crucial to the prosperity and development of a country, the improvement of lives, and the long-term stability of society. In the primary energy consumption structure of China, coal accounted for more than 50%. Although the energy structure of China is changing from coal-based to energy diversification, coal will still occupy the main position of the energy structure in the future. The energy consumption of iron and steel enterprises accounts for about 16% of the total energy consumption of industry. Coal is the essential main energy in the production process of iron and steel enterprises. Blast furnace ironmaking consumes a large amount of coal resources, so reducing coal consumption is the key to energy conservation and emission reduction.

Increasing the ratio of coal injection in blast furnaces can reduce coke consumption. With the development of coal injection technology in blast furnaces, to reduce production costs, the source of pulverized coal is expanding, and the problems such as tuyere slugging and gun plugging are gradually emerging in the corresponding injection process. The ash melting characteristics of pulverized coal injected by blast furnaces have an important influence on the combustion of coal and the change in the ash morphology of coal during gasification and liquefaction, which is also an important parameter to measure the quality of coal. A large number of scholars have done research on the melting characteristics of coal ash, such as Li et al. combined the methods of experimental research and quantum chemical calculations to study the effect of kaolin on the ash melting characteristics of Zhundong high alkali coal and the mineral evolution law during ash melting processes. Furthermore, the behavior mechanism of kaolin capturing alkali metals was also studied from the perspective of mineral microstructure features; Deng et al. used thermogravimetric analysis (TGA) to investigate the melting characteristics of Zhundong coal (ZC), coal gangue (CG), and ZC−CG blends with 10, 20, 30, 40, and 50% CG. The ash melting characteristic temperatures and mineral transformation behaviors during the ash melting process were also determined by analytical instruments; Zhou et al. used a horizontal chamber furnace to investigate the effects of two biomass ashes (corn stalk (CS) and wood pellet (WP)) on the sintering behaviors of two types of coals (high-melting Shanxi coal (SX) and low-melting Shenhua coal (SH)); Zhang et al. investigated the potassium fixation ability and ash melting characteristics during the gasification of corn stalk coke blended with coal ash in a CO₂ atmosphere; Liang et al. studied the change of mineral composition in ash and the effect of CaO on the melting characteristics of coal ash.

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by adding different contents of CaO to coal ash; Fan et al.\textsuperscript{13} investigated the effects of peanut hull (PH) ash on the initial sintering and fusion temperatures of high-melting coal ashes; Wang et al.\textsuperscript{14} used an ash fusion melting point meter and FactSage software to compare the ash melting characteristics of several common coal types and coal blends in Shougang. The melting point and high-temperature viscosity characteristics of the ash produced by the pulverized coal injection into blast furnaces before the tuyere were also investigated; and Wang et al.\textsuperscript{15} investigated the ash melting characteristics of high calcium bituminous coal, low calcium anthracite, and their blends.

Since the pulverized coal injected by the blast furnace requires a high ash melting point (>1260 °C) to avoid slagging at the tuyere, it limits the wide application of some low-ash-melting-point pulverized coal with excellent combustion performance in the field of blast furnace injection. In the process of blast furnace injection, bituminous coal and anthracite blended injection is widely used. Its advantage is to reduce fuel cost and improve the combustion rate of pulverized coal injection. Therefore, it is of great significance to study the ash melting characteristics from the perspective of the composition of coal ash and the minerals contained in it, for expanding the scope of application of coal and the mixing of low-ash-melting-point pulverized coal injection.\textsuperscript{2,16–20}

In this paper, low-cost bituminous coal with a low ash melting point was selected, and this bituminous coal was mixed with anthracite widely used by Chinese steel enterprises for mixed combustion. Experiments were carried out to study the influence of different proportions of high-ash-melting-point anthracite on the ash melting characteristics of ash produced by low-ash-melting-point bituminous coal during combustion. In addition, the mechanism of improving the coal ash melting characteristics by mixed combustion of pulverized coal was analyzed by quantum chemical calculations.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Preparation of Raw Materials. The experimental raw materials were low-ash-melting-point bituminous coal (Bulianta) with good combustion performance in Inner Mongolia of China and high-ash-melting-point anthracite (Yangquan) mainly used by steel enterprises at present. The two pulverized coals were ground to 200 meshes in an air atmosphere and dried at 105 °C for 12 h. Then, the proximate analysis and ultimate analysis of the two kinds of pulverized coals were performed, and the results are shown in Table 1. The ultimate analysis was according to the national standard (ultimate analysis of coal, GB/T31391-2015) of China. The proximate analysis was according to the national standard (proximate analysis of coal, GB/T212-2001) of China. Due to the different degrees of metamorphism of the two kinds of pulverized coals, proximate analysis and ultimate analysis were quite different. The content of the S element met the requirements of blast furnace injection (less than 0.7% was appropriate). During the process of blast furnace injection, the higher the carbon-to-hydrogen ratio (C/H), the higher the calorific value of pulverized coal and the higher the replacement ratio of coke; the higher the content of O in the ultimate analysis, the lower the degree of coal deterioration and the lower the calorific value. The replacement ratio of coke in the furnace was lower. From the results of the ultimate analysis, the carbon-to-hydrogen ratios (C/H) of bituminous coal and anthracite were 18.88 and 26.11, respectively.

Coal ash was prepared after drying according to the national standard (GB/T212-2008) of China. The ash melting characteristics of pulverized coal were measured by the determinator of melting point and melting rate according to the Chinese patent (CN 201910105185.5). The chemical composition of ash was analyzed by X-ray fluorescence (XRF). The ash melting characteristics and main chemical composition of the two kinds of pulverized coal ashes are shown in Table 2. The base-to-acid ratio (B/A) is important to see differences in the ashes. It can be seen from Table 2 that the larger the value of B/A, the lower the ash melting characteristic temperature.

2.2. Experimental Methods. The contents of Fe\textsubscript{2}O\textsubscript{3} and CaO in the ash of bituminous coal selected in the experiment were high, up to 22.92 and 31.70%, respectively. The high content of calcium iron basic oxide is the main reason for the low melting point of this bituminous coal ash. Softening means that around 30% of ash melts and particles tend to stick on surfaces. The softening temperature of this coal ash is only 1230 °C, which belongs to easy slagging coal. The anthracite and bituminous coal selected in the experiment were blended. To ensure that the fixed carbon content of the blended coal was above 70%, they were blended according to the following four proportions of anthracite and bituminous coal: 5:5, 6:4, 7:3, and 8:2. The proximate analysis of the blended coal is shown in Table 3.

It can be seen from Table 3 that the volatiles of the four different proportions of blended coal are controlled between 11 and 20%, which can meet the actual smelting needs of different blast furnaces. In addition, in this proportion, the percentage of bituminous coal ash in blended coal ash is evenly distributed between 13 and 45%, and the change of ash melting

Table 2. Ash Melting Temperature and Main Chemical Composition of Coal Ash\textsuperscript{46}

| sample       | ash melting temperature (°C) | main chemical composition (wt %) |
|--------------|-----------------------------|----------------------------------|
|              | DT | ST | HT | FT | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | CaO | MgO | SO\textsubscript{3} | B/A |
| bituminous   | 1192 | 1230 | 1252 | 1265 | 21.17 | 10.64 | 22.92 | 31.70 | 0.89 | 8.72 | 1.5 |
| anthracite   | >1400 | >1400 | >1400 | >1400 | 53.05 | 35.69 | 2.55 | 2.36 | 0.32 | 0.70 | 0.04 |

*DT: deformation temperature; ST: softening temperature; HT: hemisphere temperature; and FT: flow temperature.*
characteristics of blended coal under different proportions of bituminous coal can be studied.

Different proportions of pulverized coals were blended according to the scheme in Table 3 and burned completely at 815 °C in the muffle furnace. The ash melting characteristic temperature of the obtained samples was measured by the determinator of melting point and melting rate. During the experiment, the temperature of the samples gradually increased from 1000 to 1400 °C. In this temperature range, the DT, ST, HT, and FT of the samples were automatically recorded by the computer.

The ash samples obtained from ashing of anthracite, bituminous coal, and different proportions of blended coal at 1200 °C were analyzed by X-ray diffraction (XRD) with an MXP21VAHF type X-ray diffractometer. The determination of the main mineral components is based on the qualitative analysis of X-ray diffraction (XRD).

Based on the density functional theory (DFT) and quantum chemistry theory, quantum calculations and theoretical analysis were carried out on the physical and chemical properties of the molecular structure of the main mineral components of ash in anthracite, bituminous coal, and blended coal with different proportions.

3. RESULTS AND DISCUSSION

3.1. Effect of Different Mixing Proportions on Ash Melting Characteristics. The experimental results of ash melting characteristics of blended coal with different proportions are shown in Table 4. It can be seen from Table 4 that compared with bituminous coal, the ash melting characteristics of different proportions of blended coal are significantly improved, and the softening temperature is greater than the minimum softening temperature (1260 °C), which meets the minimum requirements of blast furnace injection for the pulverized coal ash melting point. During the experiment, the maximum temperature allowed by the experimental equipment is 1400 °C. Therefore, when the temperature reaches 1400 °C, the sample still has no melting characteristics, and the instrument records the characteristic temperature as “>1400 °C”.

It can be seen from Table 4 that after adding anthracite with a high ash melting point, the ash melting characteristics of blended coal are significantly improved. With the decrease in the proportion of bituminous coal, DT, ST, HT, and FT of blended coal are improved, indicating that blended coal has an obvious improvement effect on the ash melting characteristics of bituminous coal.

When anthracite and bituminous coal were blended in proportions of 5:5, 6:4, 7:3, and 8:2, the ash melting points (ST) of the blended coal were 1328, 1366, 1379, and 1400 °C, respectively. Compared with the bituminous coal selected in the experiment, the ash melting points of blended coal increased by 98, 136, 149, and 170 °C, respectively. Therefore, in the blast furnace smelting process, this bituminous coal is selected for injection and when this bituminous coal proportion is less than 50%, the ash melting point of blended coal is above 1300 °C, which meets the requirements of blast furnace injection.

3.2. Mineral Composition Analysis of Pulverized Coal Ash. The X-ray diffraction analysis of ash samples obtained by ashing anthracite, bituminous coal, and different proportions of mixed coal at 1200 °C is shown in Figure 1.

It can be seen from Figure 1 that the main components of the samples obtained by ashing anthracite at 1200 °C are mullite (3Al2O3·2SiO2) and anorthite (CaAl2Si2O8). The main mineral composition of the ash of bituminous coal at 1200 °C is gehlenite (2CaO·Al2O3·SiO2), and the main mineral composition of the ash of blended coal is anorthite. There is no gehlenite in the mineral components of the blended coal, which indicates that the minerals in the ash have undergone a chemical reaction during the combustion process after the two coals were blended. The high-melting-point compound mullite reacted with the low-melting-point compound gehlenite at a high temperature. The reaction produced anorthite with a melting point between the two.

3.3. Influence of the Mechanism Analysis of Blended Coal on the Meltability of Coal Ash. With the development of computational material science and the deepening of interdisciplinary research, quantum chemistry theory and calculations provide mechanism analysis and theoretical basis for further exploring the complex physical and chemical reactions between the main mineral components in the ash.

![Figure 1](https://doi.org/10.1021/acsomega.1c02621)
The Fukui function is a method based on density functional theory (DFT) to discuss the rationality of electronic theory in the chemical reaction process, and it is one of the important indicators for predicting molecular reaction activity and reaction sites.\(^{25-27}\)

Based on DFT, Parr and Yang\(^{25}\) gave the definition of the Fukui function of the electronic system.

\[
f(\tau) = \frac{[\delta\mu(\tau)]}{[\delta(\nu(\tau))]}_{N}(r) \frac{[\delta\nu(\tau)]}{[\delta(\nu(\tau))]}_{N}(r)\]

(1)

In the formula, \(\mu\) is the chemical potential, \(\nu(\tau)\) is the electron density, and \(\nu\) is the action potential of checking electrons. \(f(\tau)\) reflects the reaction site of the substance. Since the slope of the N-electron system \(\nu(\tau)\) is discontinuous, the Fukui function includes three forms of reactions.

Nucleophilic attack

\[
f^+ (\tau) = \left[\frac{[\delta\nu(\tau)]}{[\delta(\nu(\tau))]}\right]_{N}(r)\]

(2)

Electrophilic attack

\[
f^- (\tau) = \left[\frac{[\delta\nu(\tau)]}{[\delta(\nu(\tau))]}\right]_{N}(r)\]

(3)

Free radical attack

\[
f^0 (\tau) = \left[\frac{[\delta\nu(\tau)]}{[\delta(\nu(\tau))]}\right]_{N}(r)\]

(4)

In the frontier molecular orbital theory, the additional electrons in the chemical reaction process occupy the lowest unoccupied molecular orbital (LUMO) of the reactants. However, if the matter is ionized, electrons transfer from the highest occupied molecular orbital (HOMO) of the reactants. Electrons occupying the HOMO are considered to play a major role in the reaction as valence electrons in atoms. In the reaction process, the LUMO and HOMO between reactants must reach the maximum overlap so that electrons can migrate from the HOMO to the LUMO, thereby promoting the fracture of old chemical bonds and the formation of new chemical bonds.\(^{28}\)

Therefore, \(f^+\) and \(f^-\) of the Fukui function are related to the LUMO and HOMO to a certain extent. To study the distribution of the Fukui function on each atom in the N-electron system conveniently, each atom has an accurate Fukui function value. Yang simplified the Fukui function based on Mulliken layout analysis and finite difference approximation conditions\(^{21}\) as follows.

Nucleophilic attack

\[
f^+_i = q_i(N + 1) - q_i(N)\]

(5)

Electrophilic attack

\[
f^-_i = q_i(N) - q_i(N - 1)\]

(6)

Free radical attack

\[
f^0 = \frac{1}{2}[q_i(N + 1) - q_i(N - 1)]\]

(7)

where \(q_i(N + 1), q_i(N),\) and \(q_i(N - 1)\) represent the Mulliken charge values of atom \(i\) of \(N + 1, N,\) and \(N + 1\) electronic systems with the same geometric structure as that of the N-electron system, respectively. Formulas (5)–(7) are simplified Fukui functions.

The binding energy of a crystal is the energy released when free atoms (molecules or ions) combine into a crystal. Under the absolute zero condition, in addition to the zero-point vibration of atoms, binding energy is the sum of potential energy when interaction occurs between atoms.\(^{29}\) The binding energies of N atomic crystals can be expressed by the following formula

\[
E = U(r) = \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} u(r_{ij}) = \frac{N}{2} \sum_{j \neq 1}^{N} u(r_{ij}) (j \neq 1)\]

(8)

In formula (8), \(U(r)\) represents the potential energy of the interaction between two atoms with distance \(r\).

The binding energy of the crystal is related to the melting point of the crystal. For ionic crystals, the smaller the binding energy of the crystal, the lower the melting point of the material.

The crystal structures of mullite, anorthite, and gehlenite were optimized according to the DFT and plane wave pseudopotential, and then the crystal binding energy and reaction activity of the three minerals were calculated. Using the Perdew–Burke–Ernzerhof (PBE) exchange (related trends), generalized gradient approximation (GGA) method, and DNP basis set, the Brillouin zone sampling is calculated by the Monkhorst-Pack (MP) method. In the optimization process, the K point value of the three mineral crystal structures is \(3 \times 3 \times 3\).

To further explore the influence of minerals on the ash melting behavior of pulverized coal and the improvement mechanism of minerals on the ash melting characteristics of blended coal. Based on DFT and quantum chemistry theory, the physical and chemical properties of the molecular structures of the main components in anthracite ash (mullite and anorthite), bituminous coal ash (gehlenite), and blended coal ash (anorthite) were calculated and analyzed. Table 5 lists the crystal structure parameters of mullite, anorthite, and gehlenite calculated by XRD.

Table 6 lists the crystal binding energy of the three minerals obtained by calculations. From Table 6, it can be seen that the crystal binding energies of the optimized calcium anorthite, mullite, and gehlenite are \(-55534.5, -17404.3,\) and \(-74420.1\) kJ/mol, respectively. The calculation results of the crystal

| mineral   | chemical formula | binding energy, kJ/mol |
|-----------|------------------|------------------------|
| anorthite | CaAl_{2}SiO_{8}   | -55534.5               |
| mullite   | SiAl_{2}O_{5}     | -17404.3               |
| gehlenite | Ca_{2}AlSiO_{5}   | -74420.1               |

Table 5. Crystal Structure Parameters of Minerals

| mineral   | chemical formula | space group | a      | b      | c      | \(\alpha\) | \(\beta\) | \(\gamma\) |
|-----------|------------------|-------------|--------|--------|--------|-----------|---------|---------|
| anorthite | CaAl_{2}SiO_{8}  | P1          | 8.19   | 12.88  | 14.18  | 93.30     | 115.79  | 91.12   |
| mullite   | SiAl_{2}O_{5}    | B12/m       | 30.38  | 7.78   | 5.78   | 90.00     | 90.00   | 90.00   |
| gehlenite | Ca_{2}AlSiO_{5}  | P42/m       | 7.69   | 7.69   | 5.10   | 90.00     | 90.00   | 90.00   |

Table 6. Crystal Binding Energy of the Three Minerals
binding energy of anorthite are consistent with those by Ruilian Li, indicating that the calculation results are reliable.

The crystal binding energy of mullite is obviously higher than those of anorthite and gehlenite, so mullite has a stable molecular structure and its melting point temperature is also higher than those of anorthite and gehlenite. The crystal binding energy of anorthite is higher than that of gehlenite, so the melting point of anorthite is higher than that of gehlenite. Therefore, under the condition of 1200 °C, when anthracite (the main minerals of ash are mullite and anorthite) is blended with bituminous coal (the main mineral of ash is gehlenite), the mineral content of high crystal binding energy in the blended coal increases, which increases the ash melting point of the blended coal.

3.3.1. Calculation and Analysis of the Molecular Structure of Mullite. Figure 2 shows the optimal crystal structure and HOMO of mullite. Red represents the oxygen atom, purple represents the aluminum atom, yellow represents the silicon atom, and blue and yellow bulges represent the positive and negative values of the wave function.

Figure 2 shows that mullite is an aluminosilicate mineral, and its crystal structure can be regarded as evolved from sillimanite. Its cell consists of four sillimanite cells, each consisting of four Al2O3·SiO2. So, for mullite, there are four Si4+ replaced by Al3+ in 16 Al2O3·SiO2. Quantum chemical calculations of the reaction activity of mullite show that this crystal structure of mullite makes it easy to combine with electron acceptors such as cations (Na+, Ca2+, Fe2+, etc.) or ionic groups.

Figure 2 shows that Mulliken atomic population and the simplified Fukui functions (f− and f+) of the mullite crystal are also calculated, the calculation results are shown in Table S1. O(83), O(121), and their equivalent positions of mullite have the most negative atomic charges, while Al(111) and their equivalent positions have the most positive atomic charges. According to the definition of the Fukui function, the positions of the maximum values of f+ and f− are the priority attack positions of nucleophilic and electrophilic reagents. The theoretical basis of the Fukui function is that when an electron is transferred to an N-electron system, this electron will be distributed in the position where the energy of the N + 1 electron system reaches the minimum. The data in Table S1 show that the nucleophilic reagent preferentially attacks Al(111), which makes the Al−O bond break and recombine. The electrophilic reagent preferentially attacks O(83) and O(121) of mullite, which makes the Al−O bond break and recombine at this position.

By mixing coal, as electrophilic reagents, the metal ions such as Ca2+ in the basic mineral molecular structure of bituminous coal ash are easy to bond with O(83) and O(121) in the crystal structure of mullite, which makes the Al−O bond break and recombine preferentially. Michaelian found that metal cations mainly reacted with the oxygen atoms connecting two aluminum atoms in mullite to generate different structures of silicate aluminates. Zhang found that when high-melting-
point compounds were added to low-ash-melting-point coal, the main minerals in blended coal ash changed from gehlenite to anorthite. Therefore, as an electrophilic reagent, Ca\(^{2+}\) in the basic mineral structure of bituminous coal ash reacted with O(83) and O(121) in mullite, and through a series of chemical changes, it generated anorthite and other silicate aluminates. The analysis shows that after anthracite and bituminous coal are blended, basic metal ions in the blended coal ash preferentially attack O(83) and O(121) in the mullite crystal and break the Al–O bond. In the column \(f\)' of Table S1, O(83) = O(121) = 0.06, basic metal ions enter mullite. Negative ions promote the breaking of the Al–O bond from Al(111), as shown in the column \(f\)' of Table S1: Al(111) = 0.04. As O(83) and O(121) are bridging oxygen, silicate minerals in the coal ash melt react with R–O bonds (R refers to basic metal or alkaline earth metal ions) in the melt, and the oxygen ion in the R–O bond can be attracted to the vicinity of itself, resulting in the breaking of Al–O–Al bridging oxygen.

There are three types of Al–O bonds formed by Al(111). The bond lengths are as follows: the Al(111)–O(86) bond length is 0.1735 nm, Al(111)–O(30) and Al(111)–O(18) bond lengths are 0.1770 nm. Compared with the Al(111)–O(86) bond, Al(111)–O(30) and Al(111)–O(18) bonds are longer and easier to break, which makes the mullite crystal structure recombine here.

### 3.3.2. Calculation and Analysis of the Molecular Structure of Gehlenite

Figure 4 shows the optimal crystal structure and HOMO of gehlenite. Red represents the oxygen atom, purple represents the aluminum atom, yellow represents the silicon atom, green represents the calcium atom, and blue and yellow bulges represent the positive and negative values of the wave function.

Figure 4 shows that the structure of gehlenite is a tetrahedron composed of [AlO\(_4\)], [SiO\(_4\)], and weak Ca–O\(_4\) coordination, in which the volume of tetrahedral Ca–O\(_4\) is slightly larger than those of [AlO\(_4\)] and [SiO\(_4\)], thus forming a layer-like structure parallel to the (001) crystal plane.

Figure 5 shows the electronic density of state diagram of the gehlenite crystal. It can be seen from Figure 5 that in the gehlenite crystal, the valence band edge (equivalent to the HOMO) is mainly hybridized by the Al–O (the O 2p orbit hybridized with Al 3p and Al 3d orbits) to form an Al–O tetrahedron, and Si–O bond formation is weak (the O 2p orbit hybridized with Si 3p and Si 3d orbits). But the Ca–O bond has almost no orbital hybridization, so its bond formation is the weakest, which is consistent with the weak Ca–O\(_4\) tetrahedron phenomenon in the structural analysis. The bottom of the conduction band (equivalent to the LUMO) is mainly occupied by Al 3s, Al 3p, and O 2p orbits.

To distinguish the different chemical reactivities of different ions at different positions in the gehlenite structure, the Mulliken atomic population and the simplified Fukui functions \(f^-, f^+\) of the gehlenite crystal are also calculated, the calculation results are shown in Table S2. O(11), O(16), O(20), and their equivalent positions of gehlenite have the most negative atomic charges, while Al(10), Al(10), and their equivalent positions have the most positive atomic charges. The data in Table S2 show that the nucleophilic reagent preferentially attacks Al(10) and Al(10), which makes the Al–O bond break and recombine. The electrophilic reagent preferentially attacks O(11), O(16), and O(20) of gehlenite, which makes the Al–O bond break and recombine at this position.

In the gehlenite crystal, in the [AlO\(_4\)] tetrahedron where O(20) is connected to Ca(18), the bond length of Al–O(20) is the longest, 0.1827 nm, which is longer than those of the
other Al−O bonds (0.1758 and 0.1730 nm). Therefore, relatively large electron clouds will mainly concentrate on O(20) connected to Ca atoms. The Ca atom coordinated with O(20) weakens the stability of the Al−O(20) bond in the [AlO₄] tetrahedron. In the [AlO₄] tetrahedron formed by O(24), the bond length of Al(10)−O(24) is the longest, 0.1827 nm, which is longer than that of the other Al−O bonds (0.1752 nm). Therefore, relatively large electron clouds will mainly concentrate on O(24) connected to Ca atoms. The Ca atom coordinated with O(24) weakens the stability of the Al(10)−O(24) bond in the [AlO₄] tetrahedron. Metal ions are easy to capture the bonding electrons on O(20) and react with gehlenite.

When anthracite (main minerals of ash are mullite and anorthite) is blended with bituminous coal (main mineral of ash is gehlenite), the Mulliken atomic population and the simplified Fukui functions (f⁻ and f⁺) of the gehlenite shown that O(20) has the maximum f⁻ value, 0.26, which will be preferentially attacked by the electrophilic reagent, making the Ca(18)−O(20) and Al−O(20) bonds connected by O(20) break. Free electrophilic reagents generated by Ca²⁺ and its ionic groups react with mullite.

In summary, the main reason for the improvement of the ash melting characteristics of the blended coal after the addition of anthracite is that after mixing anthracite with a high ash melting point and bituminous coal with a low ash melting point at a high temperature, mullite in anthracite ash reacts with gehlenite in bituminous ash to form anorthite. The most likely reaction path of this process is as follows: mullite is easy to combine with electrophilic reagents, but it is difficult to react with nucleophilic reagents. In the ash melting process, the common basic cations (such as Ca²⁺, Fe²⁺, Na⁺, etc.) are easy to obtain electrons, which are good electrophilic reagents. Therefore, when alkaline cations such as Ca²⁺, Fe²⁺, and Na⁺ react with mullite at high temperatures, they first enter the mullite crystal through the positions of O(83) and O(121), which breaks the Al(111)−O(18) and Al(111)−O(30) bonds with relatively weak strength, resulting in the separation of octahedra and tetrahedra. The broken Al−O and Si−O bonds in the cell undergo lattice recombination, forming holes between the [Si/AlO₄] tetrahedral rings, which makes Ca²⁺ in gehlenite and other basic cations in the ash enter these holes and finally transform into anorthite.

4. CONCLUSIONS

A kind of pulverized coal is prone to slagging when used alone, but the ash melting characteristics are changed after the pulverized coal is mixed and burned. The calculation results provide theoretical support to the experimental results. The specific conclusions are as follows:

(1) When anthracite with a high ash melting point is added, the ash melting characteristics of blended coal are improved. With the decrease in the proportion of bituminous coal, DT, ST, HT, and FT of the blended coal are improved. After adding different proportions of anthracite, the ash melting point of blended coal increased by 98, 136, 149, and 170 °C, respectively.

(2) When the bituminous coal and anthracite selected in the experiment are blended for injection, the ash melting point of the blended coal with the proportion of bituminous coal less than 50% can meet the requirements of blast furnace injection. The reason for the improvement of the ash melting characteristics of blended coal is that mullite in anthracite ash reacts with gehlenite in bituminous coal ash to form anorthite with a higher melting point during combustion.

(3) The mechanism of improving the coal ash melting characteristics by mixed combustion of pulverized coal was further analyzed by the quantum chemical calculation method combined with the experimental results. The calculation results were verified with the experimental study. The reaction path of mullite in anthracite ash and gehlenite in bituminous coal to generate anorthite was proposed.

ASSOCIATED CONTENT

† Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02621.

Mulliken atomic population and the simplified Fukui functions of mullite (Table S1) and gehlenite (Table S2) (PDF)

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Notes

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