Transformation of Sodium during the Ashing of Zhundong Coal

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Abstract

Zhundong coalfield in Xinjiang is the largest integrated coal basin newly found in China. Due to the unique properties such as high volatile content, low ash and sulfur content, and high reactivity, Zhundong coal can be potentially used to supply gas fuels, liquid fuels, hydrogen, electricity and other chemical materials. However, according to practical utilization, the high alkali (especially sodium) content in Zhundong coal could induce severe problems during the combustion process, such as fouling and slagging, which influence the safe operation of the plants. It is well known that alkali metals would be volatilized at relatively low temperature. However, the existing national test standard for coal ash composition cannot completely reflect the actual content and their effect on fouling and slagging. Therefore, it is important to investigate the transformation of sodium in Zhundong coal during the ashing process. In this work, thermogravimetric analysis was adopted to determine the ignition and burnout temperatures of Zhundong coal. Coal samples were ashed at 500°C, 600°C, 700°C, 800°C, 850°C and 900°C, respectively. The element contents, phase components and microstructure of the ash were characterized with X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscope & energy dispersive spectrometry (SEM-EDS). The results show that the ignition and burnout temperatures of Zhundong coal samples are 386.5°C and 487°C, respectively, indicating that the selected ashing temperatures can ensure the complete combustion of Zhundong coal samples. The ashing temperature has a significant influence on the content and composition of sodium in ash. The total contents of sodium and chlorine decrease with the increase in the ashing temperature. At 500°C and 600°C, the main form of sodium is NaCl. At 700°C, NaAlSi\textsubscript{2}O\textsubscript{6} is observed. Further increasing the ashing temperature will promote the appearance of NaAlSiO\textsubscript{4}. 500°C can be chosen as the ashing temperature of Zhundong coal for alkali detection. Useful foundation has been laid for further study on the advanced technology for the clean and efficient utilization of Zhundong coal resource.

Keywords: Zhundong coal; ashing temperature; sodium; ash composition

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1. Introduction

Zhundong coalfield in Xinjiang is the largest integrated coal basin newly found in China. The predicted coal reserve is about 3.9×10^{11} tons, accounting for 17.8% of Xinjiang’s coal reserves (2.19×10^{12} tons) and 7.2% of China’s total coal reserves (5.56×10^{12} tons)\[1\]. Based on the existing annual coal production in China, Zhundong coalfield can serve the total consumption of the whole country for 100 years.

Due to the high volatile content, low ash content, low sulfur and high reactivity, Zhundong coal can be potentially used to supply gas fuels, liquid fuels, hydrogen, electricity and other chemical materials. However, the content of alkali metal elements (mainly sodium) in Zhundong coal is high (the mass fraction of Na_2O in ash composition analysis is no less than 2%, even higher than 10%, which is much higher than other domestic powder coal in China). According to previous researches and practical utilization in some power plants, the sodium in Zhundong coal can induce severe problems of fouling and slagging during the combustion process, impacting on the safe operation of the units. Currently, there is no effective way to solve these problems. Co-firing with other bituminous coal with lower sodium content can relieve the fouling and slagging situations, which cannot essentially solve the problems\[2\].

In the past decade, there were many pioneer researches on the sodium issue of high sodium coal. Han and Zhang[3] studied the form of sodium in coal by extracting coal samples with water, Ammonium acetate and diluted hydrochloric acid, and found that the sodium in coal can be classified as water-soluble Na, acid-soluble Na and insoluble Na. Na is mainly from the inorganic water during the long coal forming process. The water-soluble Na (also named as inorganic Na) is the main kind of Na in coal, which could be more than 50% of the total Na content in coal\[3\], but the specific form has not been confirmed. Wei[4] found that Na mainly exists in the form of NaCl crystal, while Quyn[5] found it exists as hydrated ion. Benson[6] revealed that the acid-soluble Na exists as carboxylate and coordination compound in functional groups. The insoluble Na mainly refers to aluminosilicate compounds. During the combustion of coal, the soluble Na volatilizes, some is into gaseous phase, and the other reacts with other components in coal and fixed in ash. Studies show that the soluble Na which enters to gaseous phase is the chief reason to the fouling, slagging and corrosion, thus finding a proper way to control the translation of soluble Na to fix them in ash is of great importance.

Recently, researchers have investigated the release and translation of alkali metals during the pyrolysis and combustion of high-sodium coal using the advanced test methods and instruments. Wang and Zhang[7] used X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) to detect the content and possible Na type in Zhundong coal ash at different temperatures. The results show that most Na in Zhundong coal and ash is water-soluble, and when the ashing temperature increases from 500°C to 900°C, the release of Na increases linearly, and the siliceous additives can capture Na species at high temperature. Weng[8] studied the alkali metal occurrence mode and its influence on combustion characteristics in Zhundong coal. The results demonstrate that Na content in Zhundong coal is much higher than that in other coals, and the K content is lower, which means Na is the main object to be studied. Water-soluble Na can play a positive catalytic role during the combustion process.

In order to detect Na content in coal and ash samples, confirming a proper ashing process is significant. According to GB/T 1574-2007[9], coal sample is treated at 500°C for 30 minutes, then heated up to 815°C and stay for 2 hours before Na is detected in ash. However, Na can be volatilized obviously with the increase in the ashing temperatures. Thus high-temperature-ashing could not give an accurate result. Currently, there is not a national standard for high-sodium coal ash test yet. According to ASTM standard E1755-01[10], biomass should be heated at 300°C for 30 minutes to avoid the flaming and then heated up to 575°C and hold for 2 hours in order to burn-out the residual carbon. The aim of this low-temperature-ashing process is to detect K. Fu and Wang[11] investigated the influence of ashing temperature on the ash content, composition, fusibility and volatilization characteristics. The results tell that with the increase in the ashing temperature, the content of Na in ash decreases. In order to understand the mechanism of the occurrence and transformation of Na in Zhundong coal and solve the problem induced by Na, further investigation needs to be carried out.
In this paper, a typical type of Zhundong coal was treated at different ashing temperatures from 500°C to 900°C. The element contents, phase components and microstructure of the ash samples were characterized with X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscope & energy dispersive spectrometry (SEM-EDS). The possible transformation of Na was explained and a proper ashing temperature was given for further studies.

2. Experimental Section

2.1 Fuel Characteristics

Zhundong coal used in this study was obtained from Mu Lei, Xinjiang, which was a typical type of Zhundong coal with high sodium content. Table 1 shows the proximate and ultimate analysis of the coal sample and Table 2 displays the ash compositions. The ash content of Zhundong coal was low (8.18%). The content of Na₂O in ash was 7.86%, which was much higher than the average content of coals (less than 2%) in China, and the Cl content was also rather high, accounting for 0.625%. The element composition of Zhundong coal ash indicated that Fe, S, Si in the ash is high, and Ca, Al, K, P is low.

Table 1. Proximate and ultimate analyses of Zhundong coal

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis / (wt%)</th>
<th>Ultimate analysis / (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M_ad</td>
<td>A_ad</td>
</tr>
<tr>
<td>Zhundong coal</td>
<td>14.32</td>
<td>8.18</td>
</tr>
</tbody>
</table>

*ad air dry basis, FC fixed carbon, V volatile matter, A ash, M moisture*

Table 2. Elemental composition of Zhundong coal ash (wt%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhundong coal</td>
<td>23.28</td>
<td>9.26</td>
<td>18.26</td>
<td>10.95</td>
<td>2.72</td>
<td>0.54</td>
<td>18.58</td>
<td>0.54</td>
<td>0.86</td>
<td>7.86</td>
</tr>
</tbody>
</table>

2.2 Apparatus and Method

Raw coal with particle size of 0.355-0.5 mm was sieved to 0-0.2 mm. Combined the GB/T 1574-2007[9] and E 1755-01[10], the ashing process was operated as follows: coal sample was placed on the combustion boat (less than 0.05 g/cm²). The boat was placed in a muffle furnace and the coal sample was heated to 300°C in the atmosphere of air with the heating rate lower than 10°C/min, holding for 30 minutes to avoid rapid flaming; Then it was heated continually to the target temperature of 500 °C, 600 °C, 700 °C, 800 °C, 850 °C, 900 °C and kept for 2 hours. Each experiment had three groups to ensure the repeatability, and 800°C was carried out two times to ensure reproducibility.

In order to determine the ignite temperature and burn-out temperature of Zhundong coal sample, the combustion experiment was conducted on a Netzsch STA-449F3 thermogravimetric analyzer. 10 mg Zhundong coal (the same sample with the ashing process) was dispersed on a circular alumina pan with the diameter of 6.8 mm. The sample was heated at a heating rate of 10°C/min with N₂ flow of 48 mL/min and O₂ flow of 12 mL/min. The starting and ending temperature is 30°C and 1000°C respectively. The experiment was repeated 3 times and showed great repeatability. To detect whether the low ashing process would suffer overheat problems in the exothermic combustion reaction, the 500°C and 600°C ashing processes were carried out on the thermogravimetric analyzer. To determine whether the ashes had burn out or not, the 500°C, 700°C and 900°C ashes were put in the same thermogravimetric analyzer and went through another combustion process. The experimental conditions were the same with the first combustion experiment to determine the ignition and burn-out temperatures.
2.3 Analysis Method

X-ray fluorescence (XRF, XRF-18, Shimadzu, Japan) was used to measure the total content of elements (sodium, aluminum, calcium, iron, potassium, magnesium, phosphorus, silicon, etc.) in residual ash. X-ray diffraction (XRD, D8 Advance, Bruker Co., Germany) was selected to identify the crystallized phases (including the potential mineral forms of Na in ash). The XRD system was equipped with Cu Kα radiation and run at a scan speed of 6.03 °/min with a sampling interval of 0.02 °/step over the range of 5-135°. The major crystalline phases of all fly ash were quantified using the Reference Intensity Method (RIM). Scanning electron microscope & energy dispersive spectrometry (SEM-EDS, JSM-6510, JEOL, Japan) was used to observe the morphology and analyze the surface elements of the residual ash.

3. Results and Discussions

3.1 Determine the ignition temperature and burnout temperature of Zhundong coal

Fig. 1. TG/DTG curves of Zhundong coal

Fig. 1. shows the TG/DTG curves of the combustion of Zhundong coal. The determination method is[12] as follows: draw a vertical line through the peak of DTG curve, and this line cross the TG curve at point C; through point C draw a tangent of TG curves. This curve crosses the parallel of the starting of weight loss (after the volatile period of water) on TG curve at the spot which is corresponding to the ignition temperature and the parallel of the ending of weight loss at the spot which represents the burn-out temperature. From Fig. 1, it can be determined that the ignition and burn-out temperatures of the tested Zhundong coal are 386.5 °C and 487 °C, respectively.
In order to ensure the complete ashing of samples, two experiments were carried out in thermogravimetric analyser, and the process in the thermogravimetric analyzer was the same with the experiment in muffle furnace. Fig. 2 shows the ashing process of Zhundong coal with the final temperatures of 500°C and 600°C. The results show that during the low temperature ashing process, no overheat phenomenon shows up. Also, the TG curves of 500°C and 600°C approximately coincide with each other. It can be a clue that this kind of Zhundong coal could burn out well under the low temperature ashing process. Since the lowest ashing temperature (500°C) is higher than the ignition temperature, the selected experimental temperatures in this study can ensure the ashing of sample in muffle furnace.

3.2 Effects of ashing temperatures on the content and composition of Na and relative elements in Ash

3.2.1 Total amount of main elements

Fig. 3. shows the total amount of main elements in ash samples. The ashing temperatures are 500°C, 600°C, 700°C, 800°C and 900°C. The mass ratios of the nine elements are all above 3%. Compared with Table 2, they are
also the main elements in coal ash analysis. As is shown in Fig. 3, the total amount of Na and Cl decreases with the increase in the ashing temperatures, and Ca, Si, Al, Fe and S shows an increasing trend, while Mg remains unchanged. The content of Na at the 500°C ash is 11.77%, while at 900°C ash is 6.66%, showing great difference. That’s an evidence to confirm that ashing at high temperature would lose a large amount of Na in the residual ash.

3.2.2 Transformation of crystallized phases

1-NaCl, 2-SiO₂, 3-CaSO₄, 4-CaCO₃, 5-Fe₂O₃, 6-Al₂Si₂O₁₈, 7-NaAlSi₃O₈, 8-NaAlSiO₄, 9-Ca₂SiO₄, 10-Fe₂(SO₄)₃, 11-(Ca,Na)(Si,Al)₄O₈, 12-Al₂Si₂O₅(OH)₄.

Fig. 4 shows the XRD patterns of the residual ash samples at different ashing temperatures. SiO₂, Fe₂O₃ and CaSO₄ are found in all the six ash samples. At 500°C and 600°C, the main form of Na is NaCl in the ash, and no other compound is found. The possible reason may be that the water-soluble Na hasn’t been volatized entirely from the ash, and the new compounds haven’t been generated at low temperatures. As the increase in the ash temperature, NaCl disappears and the main form of Na translates to aluminosilicate. At 700°C, NaAlSi₃O₈ (albite) shows up; when it’s up to 800°C and finally reaches 900°C, NaAlSiO₄ (nepheline) appears. Meanwhile, when the ashing temperature is 600°C, Al also comes up as Al₂SiO₁₈ (mullite); as the temperature increases, most Al is transformed into aluminosilicate. When the ashing temperature reaches 900°C, Al₂Si₂O₅(OH)₄ (kaolinite) is detected.

The release of Na during coal combustion process has two stages: at the beginning of combustion, Na in coal translates to different forms, mainly from water-soluble to acid-soluble. As the combustion continues, Na comes out as NaCl, organosodium or atoms [13]. From the perspective of thermodynamics, the volatilizable Na could react with other compounds in ash before or after the release. Temperature is the most important factor for the reaction process[14]. The possible transformation steps may be as follows[15]:

\[2\text{NaCl} + 2\text{SiO}_2 + H_2O = \text{Na}_2\text{Si}_2\text{O}_5 + 2\text{HCl}\] (1)

\[\text{Na}_2\text{SO}_4 + 3\text{SiO}_2 = \text{Na}_2\text{O} \cdot 3\text{SiO}_2 + \text{SiO}_2 + \frac{1}{2}O_2\] (2)

\[\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + \text{Al}_2\text{O}_3 = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2\] (3)
In addition, at 500°C, there is CaCO₃ in ash; when it comes to 600°C and higher, CaCO₃ decomposes and Ca₂SO₄, Ca₂SiO₄ and (Ca,Na)(Si,Al)₂O₈ (plagioclase) are formed. At different ashing temperatures, there is Fe₂O₃ all the time, and Fe₂(SO₄)₃ is detected at 850°C.

3.2.3 Morphology of ash

Fig. 5 shows SEM micrographs of Zhundong coal ash of different ashing temperatures. From these photos, it can be seen that all the six ash samples are amorphous powder, but as the ashing temperature increases, fusion gradually happens. Compared Fig. 5 (a) with Fig. 5 (f), significant effect of temperature could be noticed. The surface of 500°C ash is more rough with clear edges, while the surface of 900°C is more smooth. With naked eyes, it could be noticed that the low-temperature ash is loose power, but the high-temperature ones show agglutination. The possible explanation may be that during the higher temperature ashing process, the mineral compositions (which would contain Na, Fe, Ca, Si, Al, S, etc) of coal ash have compounded together to form low temperature eutectic content. Combined with the XRD analysis of ashes given before, as the ashing temperature becomes higher, NaAlSi₃O₈ (albite), NaAlSiO₄ (nepheline), Al₆SiO₁₈ (mullite) and Al₂Si₂O₅(OH)₄ (kaolinite) compound together with SiO₂, CaSO₄ and Fe₂O₃ to form amorphous vitreous (low temperature eutectic content) which melting point is much lower than the corresponding ashing temperatures[16].

![SEM micrographs of Zhundong coal ash of different temperatures](image)

Fig. 5. SEM micrographs of Zhundong coal ash of different temperatures

3.2.5 Relationship between Na and Cl
Fig. 6. XRF and EDS analysis of Na and Cl in Zhundong coal ash of different ashing temperatures

Fig. 6. shows the XRF and EDS analysis of the changing of mass ratio of Na and Cl during the increase in the ashing temperature. Both of the two methods are Semi-quantitative, detecting the surface chemical elements, and EDS focus on a small area. Both coherence and contradiction are shown in the two figures. With the increase in the ashing temperature, Na and Cl in both figures decrease. In Fig. 6 (a), the trends of Na and Cl show great consistency: The mass ratios of the two elements haven’t declined much during 500°C-600°C; 600 °C-700 °C is the fast decline period; 700°C-800°C shows a platform; During 800°C-850 °C, both of them decrease and the final mass ratio of Na and Cl is 6.23% and 0.04%, respectively. In Fig. 6.(b), the decrease line of Cl doesn’t show coherence with Na, but as in Fig. 6. (a), both of them decline fast during 600 °C-700 °C, and the final mass ratio of Na and Cl at 850 °C is 6.04% and 0.28%, respectively.

Although lots of investigation showes that Na and Cl in coal volatile separately during the combustion period, there are some studies demonstrating it in the opposite way. Dayton[17] used molecular beam mass spectrometer to online detect the release of gaseous alkali compounds and pointed out that for high chlorine coal, most of Na and K released as NaCl and KCl.
3.3 Determine the appropriate ashing temperature

3.3.1 Thermogravimetric Analysis of low-temperature ash

Fig. 7. shows three TG curves of ashes with ashing temperatures of 500°C, 700°C and 900°C. It can be seen that under 600°C, the difference of the three TG curves is small and there isn’t any weight lost peak. It is because the three ashes are burn out, thus the burnable composition in them is extremely low. From Fig. 7, it can also be found that the ash treated at 500°C shows two stages of weight loss (around 650°C and over 1000°C), while the 700°C and 900°C ashes only experience the high-temperature stage. These two stages of weight loss should be due to the decomposition of carbonates and sulfates in coal ash[7].

3.3.2 Determine the appropriate ashing temperature

The proper ashing temperature is rather important to detect the exact alkali content. The proper ashing temperature needs to ensure the completely burn-out of coal samples, and needs to be as low as possible in order to avoid the decrease or volatile of alkali metals. From the results above, it can be revealed that the proper ashing temperature of the studied Zhundong coal could be set as 500°C, and the ashing process could start from room temperature to 300°C and hold for 30 minutes to avoid flaming, then heat up to 500°C and hold for 2 hours. The heating rate of muffle furnace should be less than 10°C/min.

4. Conclusion

(1) The ashing temperature has a significant influence on the content and composition of alkali metals in ash. With the increase in the ashing temperatures, the contents of sodium and chlorine decrease. At 500°C and 600°C, the main form of sodium is NaCl. At 700°C, NaAlSi3O8 is observed. Further increasing the ashing temperature will promote the appearance of NaAlSiO4.

(2) With the increase in the ashing temperature, the ash becomes agglomerated, which could be attributed to the formation of lower melting point compounds. During the ashing process, NaAlSi3O8 (albite), NaAlSiO4 (nepheline), Al₆SiO₁₈ (mullite) and Al₂Si₂O₅(OH)₄ (kaolinite) can react with SiO₂, CaSO₄ and Fe₂O₃ and form amorphous vitreous, with the melting point much lower than the corresponding ashing temperatures.

(3) With the increase in the ashing temperature, the content of Na in ash decreases, while the content of Si and Al slightly increases. The volatiles of Na and Cl show some dependency, which needs further investigation.
(4) 500°C can be chosen as the proper ashing temperature for Zhundong coal used in this paper, which can both ensure the burn-out of coal and avoid the huge lost of alkali metal content during high-temperature ashing process.

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