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The Effect of Additive on Sodium Transformation and Existing Forms during Zhundong Coal Combustion

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Abstract. By means of ICP and XRF, the migration characteristics of sodium and ash fusion characteristics of the typical ZDC were studied in this article. The results indicate that most of sodium in ZDC and its ashes is in water soluble form, and most of the organically-bound sodium and few water-bound sodium is released during 500~600°C and 700~800°C. Both kaolin and silica additive can reduce the emission of sodium compounds effectively during ZDC combustion. With the increase of mixed ratio of additives, the effect is more obvious. And the reduction effect of SiO₂ is better than that of kaolin, though kaolin can turn water soluble sodium to aluminosilicate more easily which is stable and water insoluble.

1. Introduction

The coal reserves in Xinjiang Zhundong area are predicted to reach 3900 billion tons. Zhundong coal (ZDC) belongs to the low rank coal, the ash contains relatively high content of alkali metals and alkaline earth metals, resulting in strong slagging properties. Ma -YAN et.al [1] found that with the decrease of SiO₂/Al₂O₃ in Zhundong coal ash, the coal ash melting point gradually increased. SHEN Ming-ke et.al [2] found that as the proportion of kaolin blends increases, the sodium release gradually decreases, but after blending with kaolin, the melting point of coal ash first decreases and then rises which is consistent with the findings of literatures [3, 4].

In this paper, the effect of silicon-aluminum additives on the release of sodium were studied, which provide reference for large-scale application of Zhundong Coal.

2. Experimental part

2.1. Coal quality analysis

Proximate analysis and chemical compositions of ash samples for ZDC were shown in Table 1, it can be seen that ZDC is rich in alkali metals and alkaline earth metals. Though the ash melting temperature is as high as 1360°C, and there are serious slagging and fouling phenomena during combustion in power plants.



Table 1. Proximate analysis and chemical compositions of ash samples for Zhundong coal

Proximate analysis/%				chemical compositions of ash samples%									
M_t	A_{ad}	V_{ar}	FC_{ad}	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	SiO_2	SO_3	K_2O	Na_2O	ST/°C
29	5.12	29.47	63.75	8.01	7.36	24.54	6.96	0.99	14.3	32.8	0.4	4.65	1360

2.2. Ashing experiment and sample analysis

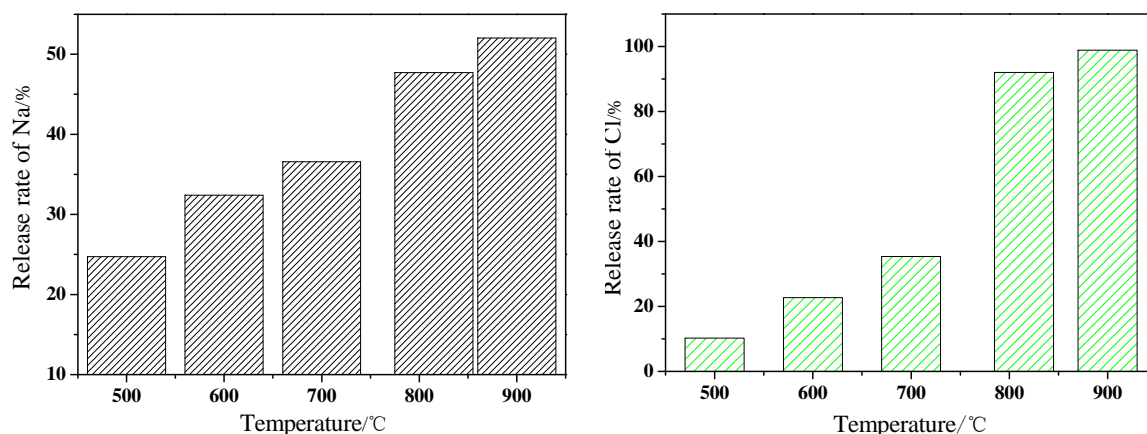
This article refers to the analysis method of coal industry 《GB/T 212—2008》 and adopts gradient method to obtain ash samples: Within one hour, the temperature was increased from room temperature to 500°C, left for 30 minutes, and then the target temperature was reached at a temperature increase rate of 10 °C/min. The sample was heated at the target temperature for one hour. The sample preparation temperatures were 500°C, 600°C, 815°C, 1000°C, 1150°C, and 1250°C, and the blending ratio of additives and raw coal was 0%, 3%, 6%, and 9%.

In this paper, ultra-pure water and dilute hydrochloric acid were used to pretreat ash samples. ICPE-9000 manufactured by Shimadzu Corporation was used to determine the water-soluble and acid-soluble contents of alkali metals. The Bruker S4-Pioneer X-ray fluorescence spectrometer (XRF) was used to determine types and contents of elements in ash samples.

3. Results and Discussion

3.1. The Existing Forms of sodium in ZDC and the Migration of Na during ZDC Combustion

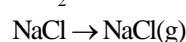
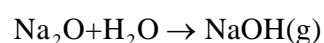
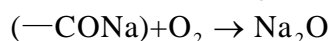
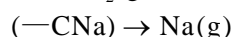
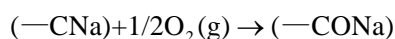
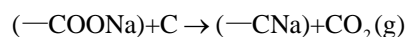
In order to determine the migration law of sodium during coal combustion, the element analysis of ash samples produced at 500~900°C was analyzed by XRF. The changes of the content of Na and Cl elements under different ash forming temperatures were calculated, as shown in Figure 2.

**Figure 1.** The changes of the content of Na and Cl elements under different ash forming temperatures

As can be seen from Figure 1, the release rate of sodium in coal increases with the increase of temperature, especially at the temperature of 700~800°C, the release rate of sodium increases sharply, and the release amount of sodium at 900°C accounts for 53% of the total. As can be seen from Fig. 2, the release of Cl in coal is mainly at 700~800 °C, and the release rate increases from 35% to 95%, and has been completely released at 800~900 °C.

Therefore, it is presumed that the sodium release process is as follows: before 500°C, it is the stage of volatilization precipitation and carbon burning. The sodium released at this stage is all organic sodium and partially hydrated sodium; in the temperature range of 500°C to 600°C, a large amount of hydrated sodium ions emancipated that combined with compounds by Van der Waals forces in the coal, resulting in a significant increase in the sodium release rate at this temperature range. This is

consistent with the results reported in [5, 6]; at the temperature range of 700~800°C, the sodium release rate is 36% increased to 50%, combined with the analysis of release characteristics of Cl element shown in Figure 2, it is presumed that the Cl element in the raw coal may be released from 700 to 800°C, combined with sodium to form NaCl (g). From the above analysis, combined with the literature [7, 8], this article assumes that the sodium release reaction during coal combustion is as follows:



Based on the analysis results of XRF and ICP-9000, the percentages of water-soluble sodium and water-insoluble sodium in ash samples produced at 500~900°C are shown in Figure 2.

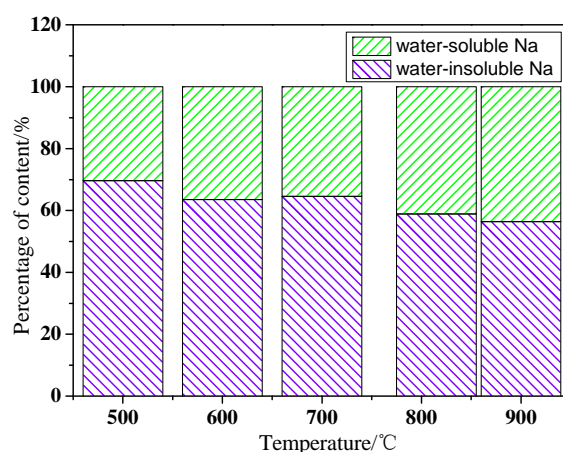


Figure 2. Influence of ash forming temperature on the percentage of sodium in different forms

In Figure 2, it can be seen that water-soluble sodium is the main existing form in the ash samples with different making temperatures. The proportion of water-soluble Na is gradually reduced with the increase of temperature. Because of the high content of SO_3 in ZDC, it is speculated that the water-soluble Na which has not been released at 900°C is mainly in the form of Na_2SO_4 , which is not easy to emancipate because of its good stability. With the emancipation of other forms of sodium, the percentage of water-insoluble sodium increases.

3.2. Effect of additives on sodium release and occurrence during combustion of ZDC

Studies have shown that the greater the content of Si and Al in coal, the more difficult the sodium is to be discharged. The ZDC is mixed with 3%, 6%, 9% SiO_2 and kaolin respectively, then the ash samples are made at different temperatures. Using XRF and ICPE-9000 to analyze the total sodium and the content percentage of water-soluble sodium in the ash samples, the effect of SiO_2 and kaolin on the release rate and the existing form of sodium during the coal combustion can be obtained, as shown in Figure 3.

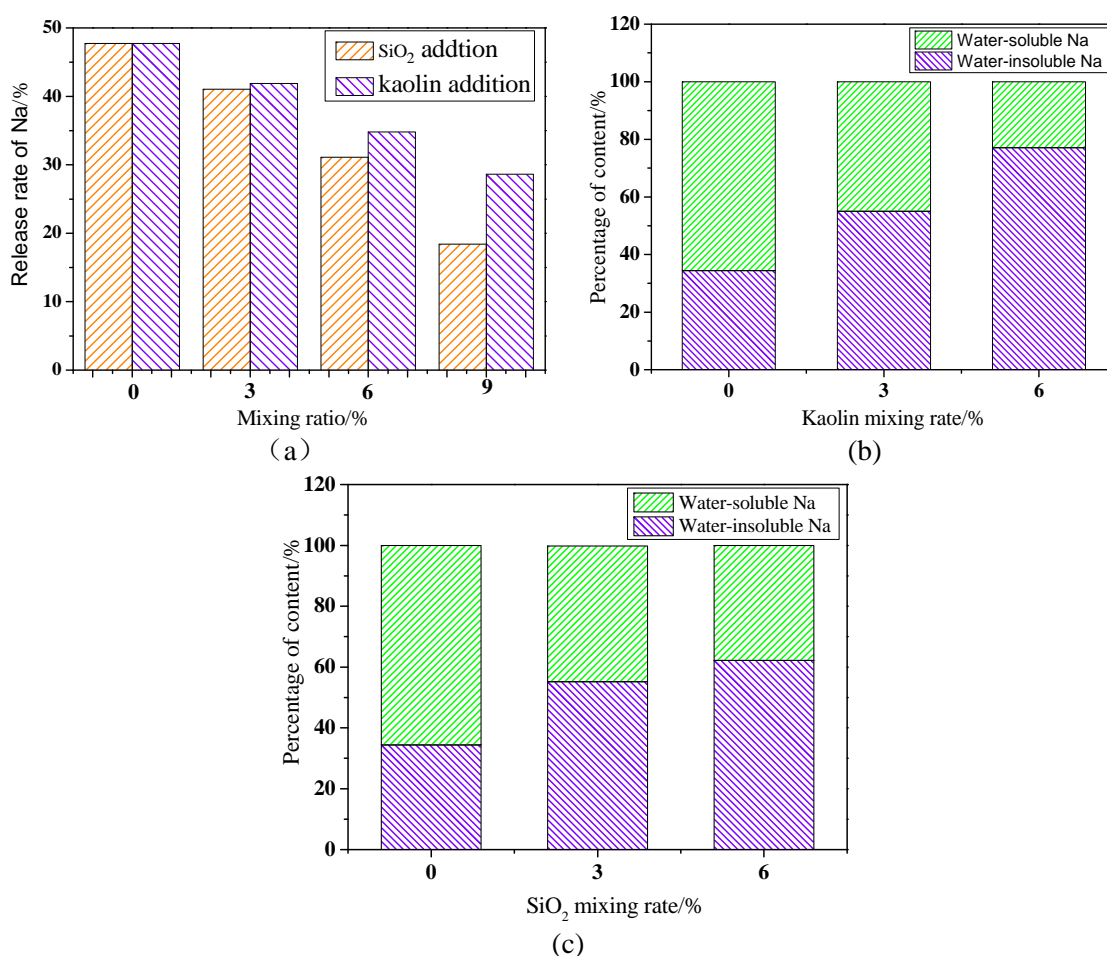
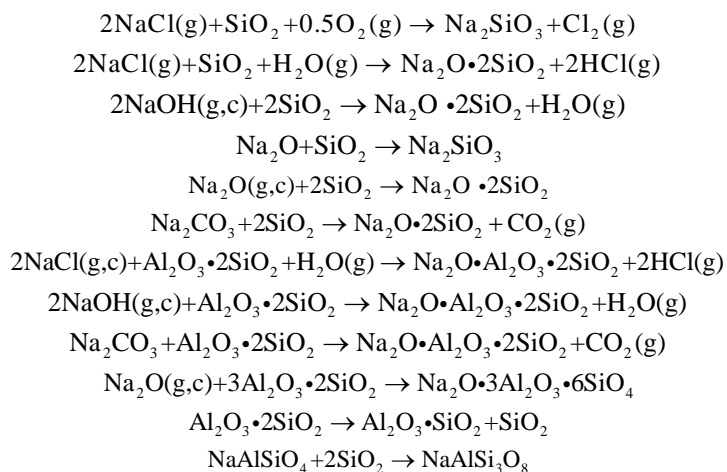


Figure 3. Effect of additives on Na release and occurrence form in ZDC

From Figure 3 (a), it can be seen that the release rate of sodium decreases obviously with the increase of SiO₂ or kaolin additive mixing ratio, which is because the possibility of Na exposure to SiO₂ or kaolin is enhanced during ZDC combustion, so the release rate of sodium was suppressed. Contrasting two kinds of additives, it can be found that the effect of SiO₂ is better than kaolin, especially when the mixing ratio reaches 9%. This may be due to the reaction of SiO₂ and ash components to produce low temperature eutectic matters, which inhibits the release of sodium in ash, kaolin reacts with sodium to produce a high melting point silicon aluminum salt. In addition, kaolin can also react with Na₂SO₄ in ash before 800°C [9], which affects the reaction between kaolin and volatile sodium salts.

As shown in Figure 3 (b) (c), the percentage of water soluble sodium decreases with the increase of mixing ratio of SiO₂ or kaolin. This is because: firstly, the reaction of SiO₂ and sodium in ash will produce Na₂Si₂O₅ that is not soluble in water, and produce Na₂SiO₃ meanwhile that is soluble in water. With Al₂O₃ participating in the ash sample, sodium can produce a stable silicon aluminate insoluble in water with SiO₂. In addition, the reaction of Sodium and SiO₂ in the presence of Fe, Ca, Mg and other substances will produce low temperature eutectic matters, such as calcium silicate, diopside, etc. Secondly, sodium reacts with kaolin to form water-insoluble salts such as Na₂O·Al₂O₃·2SiO₂, NaAlSiO₄, NaAlSi₃O₈ and other substances [10, 11], resulting in a continuous decrease in the percentage of water-soluble sodium. However, with the increase in the amount of additives, the reaction to produce water-insoluble sodium is basically completed. The chemical reaction that inhibits sodium release after adding SiO₂ and kaolin is presumed:



4. Conclusion

Most of sodium is in water-soluble form in ZDC and ZDC ashes. And most of the organically-bound sodium and few water-bound sodium in ZDC is released during 500~600°C and 700~800°C. Both kaolin and silica additive can reduce the emission of sodium compounds effectively during ZDC combustion. With the increase of mixed ratio of additives, the effect is more obvious. And the reduction effect of silica is better than that of kaolin, though kaolin can turn water soluble sodium to aluminosilicate more easily which is stable and water insoluble. By comparing two kinds of additives, it can be found that kaolin is more suitable to be used as a slagging inhibitor of ZDC, but it needs controlling the blending ratio strictly.

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