

Article

Co-Firing Zhundong Coal with Its Gangue: Combustion Performance, Sodium Retention and Ash Fusion Behaviors

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Abstract: Fouling and slagging are intractable ash-related problems for boilers burning high-sodium coals (HSC) to produce electricity or heat. Reduction and resource utilization of solid waste, coal gangues, is urgent because of stringent environmental regulations and economic benefits. Based on the sodium-rich character of Zhundong coal (ZDC) and the mineralogical features of the coal gangues (ZDG), this work investigated their co-firing performance, the sodium retention behaviors as well as the slagging and fouling tendency of the ashes. Results show that combustion performance of ZDC is not reduced despite of the lower reactivity of ZDG. The co-firing reaction follows the 3D diffusion model (cylinder symmetry) which probably reflects the gas diffusion of oxygen to combustible matter. During co-firing, the enriched silica and alumina components in ZDG efficiently react with the alkali and alkaline earth metals (sodium, magnesium and calcium) in ZDC to form complex minerals, thus effectively capturing and retaining sodium. The slagging and fouling propensity of ashes are notably reduced. Overall, co-firing provides an alternative means to solve the ash slagging and fouling issues, and also for the reduction and resource utilization of coal gangues.



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Keywords: coal gangue; co-firing performance; sodium retention; slagging and fouling

1. Introduction

Coal gangues are solid wastes produced from the coal mining and washing process, and their quantity amounts to 10–15% of raw coal production. The estimated annual increase of coal gangues reaches 0.37–0.55 billion tons based on the production of coal for China in recent years. Worse still, the current accumulation of coal gangues reach 4.5–5.0 billion tons [1]. The enormous coal gangue hills occupy great a quantity of soil and cause serious environmental impacts such as soil pollution (heavy metals) and air pollution (spontaneous combustion) [2–4]. Thus, the disposal and minimization of coal gangues is urgently required. By far, the most effective and comprehensive utilization of coal gangues is to burn them as low-grade fuels for power generation in China. However, owing to their low volatile and high ash content, coal gangues are difficult to burnout and their flame stability is poor. Additionally, the thermal efficiency of boilers burning coal gangues is low due to their low calorific values. Co-firing is proven effective for enhancing the combustion performance of coal gangues [5–7].

The typical components of coals gangues are 50–70 wt.% clay minerals (kaolinite, illite, montmorillonite, boehmite, etc.), 20–30 wt.% quartz and 10–20 wt.% carbon. Their chemical compositions are mostly SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO, among which SiO₂ accounts for about 50%. Both SiO₂ and Al₂O₃ are widely reported as active components for capturing gaseous sodium during combustion, making coal gangues potential additives for alleviating ash-slagging or fouling problems during ZDC combustion [8–10]. Besides, the high volatile content and high reactivity of ZDC probably compensates for the deficiency of coal gangues in calorific values, burning rate and flame instability.

Zhundong coal field, located at the Junggar Basin of northwest China, receives extensive attention ascribed to its large coal reserves (estimated to be 164 Gt) [11]. The rank of Zhundong coals (ZDCs) varies from lignite to sub-bituminous coal, and they are deemed as suitable fuels for heat and power generation because their low ash and sulfur content and high volatility and reactivity [12,13]. Efficient and clean burning of ZDC is significant for the improving the local economy as well as ensuring energy security. Nevertheless, ZDCs are widely known as high alkali coals (especially sodium), and the sodium content in their ashes mostly exceed 2 wt.% (some even reaches 10 wt.%), which is far greater than that of common thermal coal (≤ 1 wt.%). The sodium content causes severe ash-related problems (e.g., slagging, fouling and corrosion) and greatly restricts large-scale and safe burning of ZDC in boilers [14–18].

Extensive efforts have been made to elucidate the mechanism and the possible solutions to alleviate the ash-related problems (slagging and fouling) [15,19–22]. Based on the previous literatures, Na easily sublimates into the gas phase during combustion [17,23], while Cl and S in the coal combined with gaseous Na and forms NaCl or Na₂SO₄ at high temperatures [24,25]. The Na-containing compounds promote the formation of a sticky inner layer, which is closely related to the ash-fouling problems [26]. From this point, the inhibition of Na volatilization into the gas phase during combustion is crucial to alleviate the ash-fouling problems. On the other hand, the slagging problems are largely due to the low melting temperatures of the ashes, which are mainly composed of Si, Al and Ca according to Shi et al. [27]. Besides, the presence of iron also exacerbates the ash-fouling and slagging problems, especially under reducing atmosphere [28].

Currently, many thermal plants tend to ameliorate the problems by co-firing with coals with lower sodium content, but this further increases the fuel cost for electricity production [29]. Unfortunately, despite of various methods proposed to alleviate the ash-fouling and slagging issues such as blending combustion [30], leaching [31] and using additives [32,33], these problems are still far from being completely solved. The keys for eliminating sodium-related ash problems are to inhibit the migration of sodium into its gas phase (flue gas) and to retain more sodium in the ashes, which probably reduces the viscosity of fly ash and raises the ash fusion temperature of ashes in boilers [24,29,34]. To this end, some thermal plants take the measure of adding minerals (e.g., kaoline and montmorillonoid) that are rich in silica and alumina into boilers [35–37]. Despite of its mediocre effectiveness, the addition of these minerals not only raises cost but also wastes natural resources.

Circulating fluidized bed (CFB) technology is proved suitable for burning low-grade fuels thanks to its high efficiency, low pollutant emission and good economy [38–40]. HSC can be blended with coal gangues and burnt in CFB to establish stable ash circulation flow. An obvious merit is the relatively low operating temperatures (800–900 °C) that possibly prevents the ash from melting, softening and deforming. Moreover, the reactions among minerals in the blended fuels or their ashes probably capture sodium vapor and retain it into ashes, or produce sodium-containing minerals that are refractory, thus alleviating the intractable ash-related problems. Therefore, co-firing HSC with coal gangues in CFB boilers under appropriate controls probably achieves efficient and safe burning of HSC, while also realizing the disposal and resource utilization of coal gangues simultaneously. Still, the effect of co-firing on combustion performance, slagging and fouling properties of the resultant ashes remains to be clarified.

Taking into account of the above considerations, this work aims to examine the combustion behavior of the blended fuels to evaluate the co-firing performance of ZDC and ZDG under a relatively low temperature (900 °C). Moreover, the effect of co-firing on the slagging and fouling propensity was investigated to verify if co-firing ZDG can facilitate inhibiting the ash-related problems of ZDC. The results can be useful for the practical co-firing HSC and coal gangues in commercial CFB boilers.

2. Experimental

2.1. Materials

A coal and coal gangue sample collected from Zhundong region were used as fuels and denoted as ZDC and ZDG, respectively. The samples were crushed and ground to less than 0.2 mm before being dried under vacuum at 80 °C overnight. Proximate and ultimate analyses results were listed in Table 1. Their ashes were analyzed according to the Chinese national standard GB/T 30732-2014 and the results were presented in Table 2.

Table 1. Proximate and ultimate analyses of ZDC and ZDG.

Sample	Proximate Analysis/(wt.%)				Ultimate Analysis/(wt.%)				
	M _{ad}	Ash _{ad}	VM _{ad}	FC _{ad}	C _{daf}	H _{daf}	N _{daf}	O _{daf} *	S _{daf}
ZDC	13.4	3.6	29.5	53.6	79.07	3.76	0.61	15.99	0.57
ZDG	1.9	66.9	10.6	20.6	79.77	3.64	1.09	14.14	1.35

M, moisture; FC, fixed carbon; ad, air-dried basis; daf, dry and ash-free basis; VM, volatile matter; * by difference.

Table 2. Ash composition of ZDC and ZDG.

Sample	Mass Fraction (wt.%)										
	CaO	SiO ₂	Al ₂ O ₃	SO ₃	Na ₂ O	MgO	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	K ₂ O	Others
ZDC	38.71	5.66	7.31	15.32	8.35	15.81	7.24	0.03	0.36	0.13	1.08
ZDG	4.86	57.76	22.99	0.67	2.48	1.94	5.60	0.00	0.97	1.88	0.85

2.2. Combustion Tests

Combustion test of ZDC and ZDG alone, as well as co-combustion were performed on a thermogravimetric analyzer (STA 449F3, Netzsch, Germany). In each run, approximately 10 mg sample with a particle diameter less than 74 µm was charged into a corundum crucible, which was heated from ambient temperatures to 900 °C at 10 °C/min in 100 mL/min air. It was found that all samples were completely burnt during the temperature ramping step. Each run was duplicated to reduce the experimental error. For the co-combustion tests, the ratio of ZDG in the blended fuels varied at 5%, 10%, 20%, 50% and 80%, respectively.

Several combustion indexes were used to evaluate the co-firing performance. The characteristic temperatures including ignition temperature (T_i), peak temperature with maximum weight loss rate (T_p) and burnout temperature (T_f) were determined according to previous works [41,42]. The comprehensive combustion index (S_N) was defined as with Equation (1).

$$S_N = \frac{DTG_{max} \cdot DTG_{mean}}{T_1^2 \cdot T_3} \quad (1)$$

where DTG_{max} and DTG_{mean} were the maximum and mean value of weight loss during combustion, and the unit of S_N was ($K^{-3} \cdot min^{-2}$).

Carbon conversion (X_c) was used to eliminate the interference of minerals or ashes on combustion reactivity

$$X_c = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

where m_0 , m_t and m_∞ are the initial, instantaneous and final weight of the sample during combustion.

2.3. Chemical Composition and Morphology Analyses of Ashes

The mineralogy of the fuels and their ashes were examined with X-ray diffractometer (D8 ADVANCE, Bruker, Karlsruhe, Germany) with Cu K α radiation (40 kV, 40 mA, K α_1 = 0.15408 nm). The samples were scanned with a step size of 0.02° at 5°(2 θ)/min over 10–90°. The ash compositions were analyzed by X-ray Fluorescence Spectrometer

(ARL Advant'X Intellipower™ 3600, ThermoFisher Scientific, Waltham, MA, USA). Their morphology was characterized with scanning electron microscopy (JSM-6490LV, JEOL, Shoshima, Japan). The ash-melting behaviors were investigated according to the Chinese standard GB/T212-2008, and the characteristic ash fusion temperatures including initial deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) were determined. The detailed procedures were referred to previous work [8].

2.4. Prediction of Slagging and Fouling Tendency

To evaluate the slagging and fouling propensity of the ashes, various indexes including slag viscosity (S_R), the ratio of basis to acid component in ash ($R_{b/a}$), slagging index (R_s), wear index (H_m) and fouling index (F_u) were calculated with Equations (3)–(7) based on the previous studies [8,43,44].

$$S_R = \frac{SiO_2}{SiO_2 + CaO + MgO + Fe_2O_3} \times 100 \quad (3)$$

$$R_{b/a} = \frac{Fe_2O_3 + K_2O + CaO + Na_2O + MgO}{SiO_2 + Al_2O_3 + TiO_2} \quad (4)$$

$$R_s = R_{b/a} \times S_{t,d} \quad (5)$$

where $S_{t,d}$ is the sulfur content (%) of the fuels on day basis.

$$H_m = \frac{A_{ad}}{100} (SiO_2 + 0.8Fe_2O_3 + 1.35Al_2O_3) \quad (6)$$

where A_{ad} is the ash content on the air-dried basis.

$$F_u = R_{b/a} \times (Na_2O + K_2O) \quad (7)$$

3. Results and Discussion

3.1. Co-Combustion Performance

The weight loss behaviors of ZDC, ZDG and the mixed fuels during combustion are presented in Figure 1. Clearly, with the completion of combustion at approximately 600 °C, the weight loss for ZDC and ZDG reaches 88.5% and 37.9%, respectively. Additionally, the weight loss gradually decreases with rising ratios of ZDG, e.g., with the ratio of ZDG at 5%, 10%, 20% and 50%, the weight loss is 86.1%, 83.5%, 78.9% and 62.0%, respectively. This is expected, as ZDC contains significantly higher VM and FC content than ZDG as shown in Table 1. Figure 1b shows the DTG curves for the combustion test. The weight loss rate and peak temperatures are related to the property (e.g., VM and FC) of the blended fuels. Generally, with the rising ratio of ZDG, the weight loss rate decreases. The peak temperature of ZDG is obviously higher than that of ZDC, further verifying the lower burning reactivity of ZDG. Intriguingly, co-firing at certain ratios (e.g., 5% ZDG) not only accelerates the burning rate, but also reduces the peak temperature, exhibiting positive interactions and synergisms of co-firing, which is consistent with the reports in the previous study [45].

The characteristic parameters of combustion derived from the TG and DTG curves are exhibited in Figure 2. The ignition temperature (T_i) varies slightly at 5–80% ZDG, indicating that co-firing ZDG with ZDC does not inhibit or retard ignition of the blended fuels. This is important for the continuous operation of CFB boilers. As expected, the peak (T_p) and burnout (T_f) temperatures increase with rising ZDG ratios because of its lower reactivity. As expected, the S_N value decreases due to the same reasons. This is consistent with the components, especially the content of combustible substances (VM and FC) of the blended fuels. Herein, the ratio of $((VM_{ad} + FC_{ad})/Ash_{ad})$ is calculated and shown in Figure 2. Clearly, its value monotonously decreases with the rising ratios of ZDG. From the practical viewpoint, too much coal gangue undoubtedly lowers heating values

and thermal efficiency of CFB boilers and also deteriorate its stable operation. Thus, the co-firing ratio should be kept at reasonable values (e.g., 10% or 20%), depending on the overall performances of boilers.

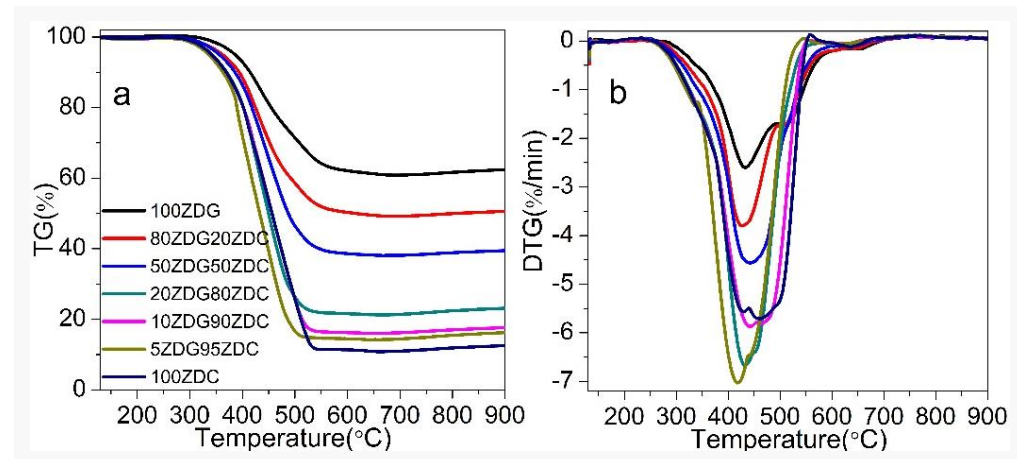


Figure 1. TG (a) and DTG (b) curves of ZDC co-firing with ZDG.

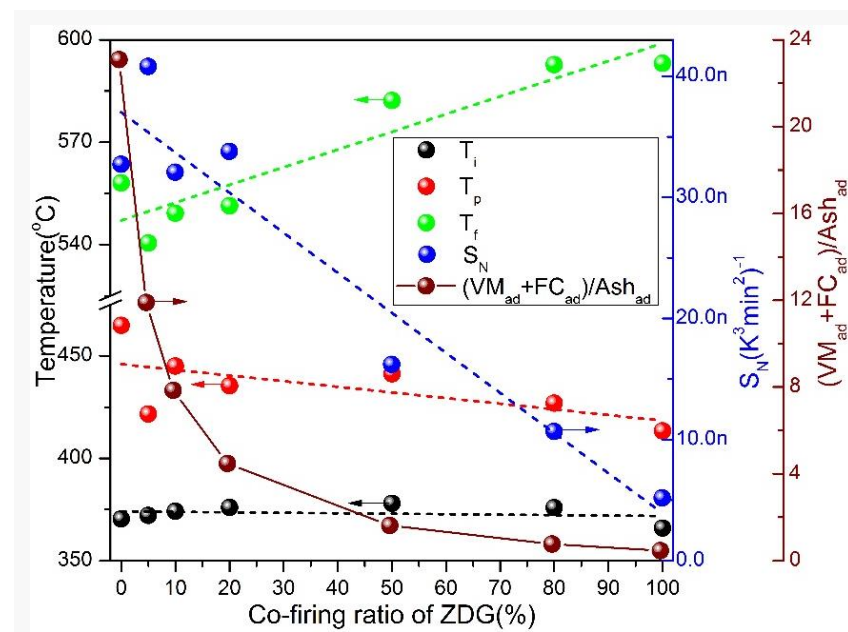


Figure 2. Characteristic parameters of combustion.

The carbon conversion (X_C) during combustion was calculated with Equation (2). Using the widely adopted integral method to analyze the non-isothermal kinetic data, the conversion curves were fitted to determine the most probable reaction mechanism [46]. The fitting results were shown in Figure 3. The curves well follow the Ginstling-Brounshtein equation and the proper reaction mechanism was confirmed as the 3D diffusion model (cylinder symmetry), judging from the high correlation coefficient. It can be speculated that the co-firing is controlled by the gas diffusion process instead of chemical reaction. Theoretically, this is a typical gas-solid heterogeneous reaction, and its rate is dependent on various factors such as gas diffusion rate, heat transfer and chemical reaction. The fitting result indicates that the combustion process is controlled by the gas diffusion process, especially the diffusion of oxygen to the carbon matrix in fuel. As the powder sample is heaped in the small corundum crucible during combustion, the oxygen in air flow must diffuse into the carbon matrix through the gas layers of volatile matter and CO_2 that evolved from the fuel to initiate the combustion of char (or FC), thus the amount and

layer thickness of volatile matter (VM and CO₂) in the crucible notably affect the diffusion rate. Alternatively, the thickness of ash layers formed from combustion increases with the extension of burning time, therefore increasing the resistance of gas diffusion.

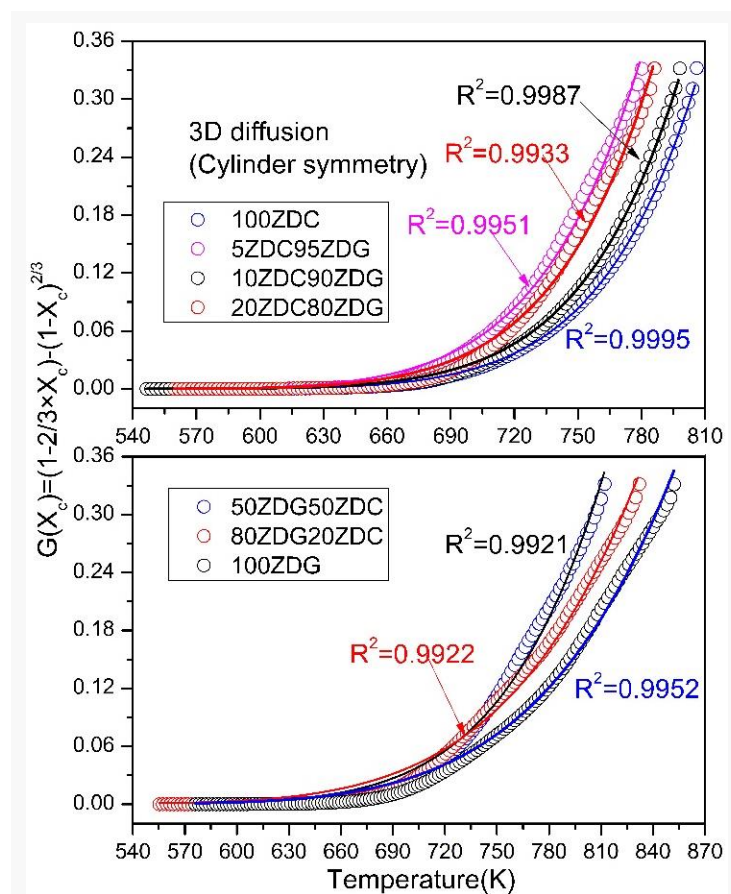


Figure 3. Mathematical fitting co-firing curves with 3D diffusion (cylinder symmetry) model.

From the curve-fitting results (Figure 3), the 'activation energy (E_a)' can be obtained and the results are shown in Figure 4. Surprisingly, the E_a values decrease with the increase of ZDG ratio during co-firing. Based on the discussions above, it can be deemed that the values of E_a actually reflect the diffusion resistance of oxygen to the carbon matrix rather than the combustion reaction of the carbon matrix. A higher co-firing ratio of ZDG reduces the diffusion resistance of oxygen molecules to the carbon matrix. This is expected as ZDG contains remarkably lower VM content than ZDC, and mixtures with a higher ratio of ZDG generate a thinner gas layer, thus reducing the gas diffusion resistance (as briefly shown in the scheme of Figure 4). In addition, the accumulated AAEM components that can catalyze combustion of the blended fuel also contributes to the reduced activation energies. The lower activation energy for combustion is potentially favorable for the practical operation of CFB using the blended fuels. Besides, it is probable that more porous structures are formed with higher co-firing ratios of ZDG that facilitates gas diffusion, thus lowering E_a values during co-combustion tests.

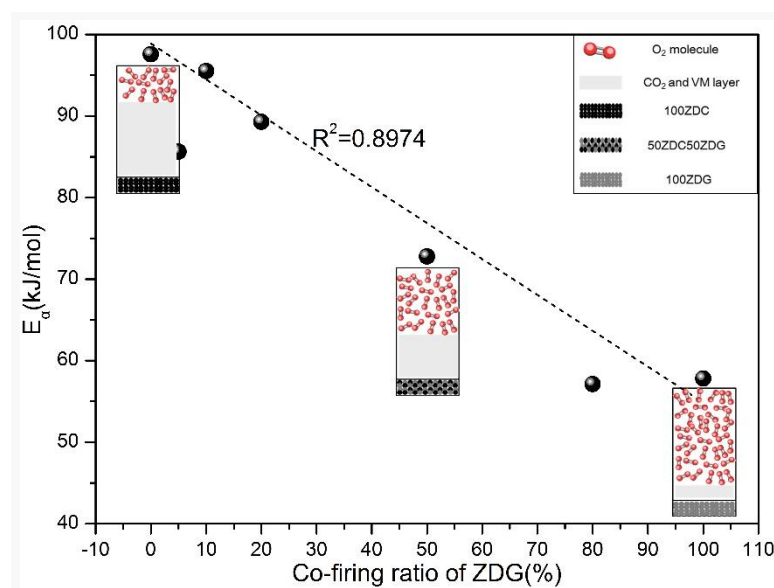


Figure 4. Activation energy of co-firing ZDC and ZDG.

3.2. Ash Compositions and Mineralogy

XRD patterns of the mineral components of the fuels and ashes are displayed in Figure 5, and the assignments of diffraction peaks are presented in Table 3. ZDC exhibits few diffraction peaks due to its low ash content and strong diffraction peak of amorphous carbon at 25.30° . Comparatively, ZDC ash shows distinct diffraction signals of lime (CaO), anhydrite (CaSO_4) and calcium ferrate (CaFe_2O_4), and this is consistent with its high CaO (38.71%) as shown in Table 2. Comparatively, ZDG and its ash show similar diffraction patterns, and their dominant components are quartz (SiO_2) and diopside. Semi-quantitative analysis of the samples were performed and the results were listed in Table 3. The fitted XRD patterns match well with the raw XRD patterns as shown in Figure 6 (taking 100ZDG ash as an example), verifying the reliability of the quantitative results (presented in Supplementary Materials). Comparatively, ash from mono-combustion of ZDC or ZDG comprises simple compounds such as quartz, lime and anhydrite, while the ashes derived from co-firing are more complicated, e.g., akermanite, enstatite and anorthite sodian. The variations confirm the interactions among the ash components during combustion. In addition, the calcium-containing species gradually decreases while those of silica and aluminum-containing components increase with rising co-firing ratios of ZDG. This trend is in accordance with the ash compositions (show in Table 2), and these variations probably change the ash fusion temperatures thus affecting the fouling or slagging behaviors. In the following section, the effect of co-firing on sodium retention and ash fusion behavior is investigated and discussed.

Table 3. Quantitate results of the XRD analysis.

Sample	Minerals	Characteristic Peak Position ($^\circ$)	Relative Content (%)
100ZDC ash	Aluminum oxide (Al_2O_3)	25.61, 37.60, 52.19	0.2
	Lime (CaO)	32.31, 37.51, 54.03, 64.43	8.5
	Anhydrite (CaSO_4)	38.78, 40.97, 48.83	30.2
	Calcium ferrate (CaFe_2O_4)	33.69, 48.37, 52.99, 62.81	61.1
5ZDG 95ZDC ash	Gehlenite ($4\text{CaO} \cdot 2(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)$)	24.14, 29.29, 31.40, 36.95, 52.40	98.3
	Silicon diphosphate ($\text{SiO}_2 \cdot \text{P}_2\text{O}_5$)	20.67, 23.27, 26.70, 33.95	1.7
10ZDG 90ZDC ash	Akermanite ($4\text{CaO} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3(\text{SiO}_2)$)	22.97, 23.99, 29.16, 31.37, 35.63	28.4%
	Quartz (SiO_2)	20.79, 26.65, 36.65, 42.36, 45.79, 50.025, 59.92, 67.98	3.5%
	Augite ($4\text{CaO} \cdot \text{FeO} \cdot 3(\text{MgO}) \cdot 8(\text{SiO}_2)$)	27.71, 29.95, 35.89	68.0%

Table 3. Cont.

Sample	Minerals	Characteristic Peak Position (°)	Relative Content (%)
20ZDG 80ZDC ash	Quartz (SiO_2)	20.79, 26.65, 36.65, 42.36, 45.79, 50.025, 59.92, 67.98	21.4%
	Diopside ($\text{CaO} \cdot \text{MgO} \cdot 2(\text{SiO}_2)$)	29.86, 30.87, 35.63	60.0%
	Enstatite ($12\text{MgO} \cdot 2(\text{Fe}_2\text{O}_3) \cdot 16(\text{SiO}_2)$)	27.95, 29.96, 35.07	18.6%
50ZDG 50ZDC ash	Quartz (SiO_2)	20.79, 26.65, 36.65, 42.36, 45.79, 50.025, 59.92, 67.98	52.0%
	Anorthite sodian ($0.5(\text{Na}_2\text{O} \cdot \text{CaO} \cdot 1.5(\text{Al}_2\text{O}_3) \cdot 5(\text{SiO}_2))$)	21.10, 27.88, 42.35	48.0%
80ZDG 20ZDC ash	Quartz (SiO_2)	20.79, 26.65, 36.65, 42.36, 45.79, 50.025, 59.92, 67.98	28.7%
	Anorthite sodian ($0.5(\text{Na}_2\text{O} \cdot \text{CaO} \cdot 1.5(\text{Al}_2\text{O}_3) \cdot 5(\text{SiO}_2))$)	21.10, 27.88, 42.35	71.3%
100ZDG ash	Quartz (SiO_2)	20.79, 26.65, 36.65, 42.36, 45.79, 50.025, 59.92, 67.98	65.5%
	Diopside ($\text{CaO} \cdot \text{MgO} \cdot 2(\text{SiO}_2)$)	29.86, 30.87, 35.63	34.5%

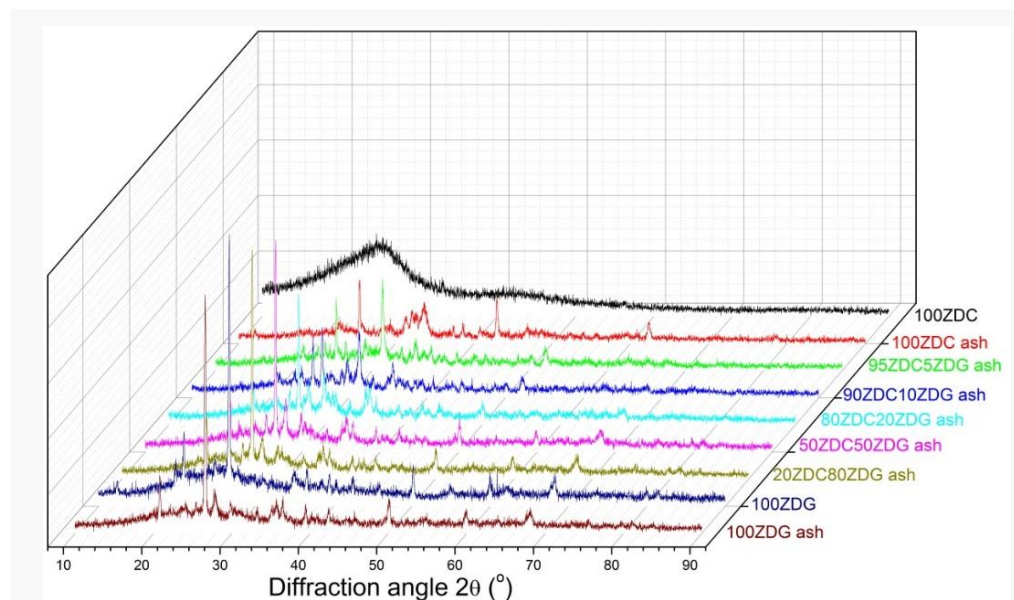


Figure 5. XRD patterns of the fuels and the ashes.

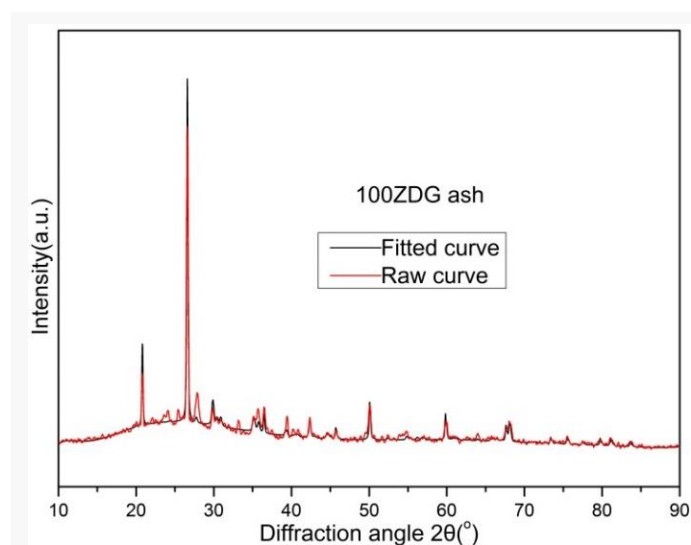


Figure 6. Raw and fitted XRD patterns of ZDG ash.

An objective of co-firing ZDC and ZDG is to reduce the migration of sodium into the gas phase, which is responsible for the fouling and slagging problems. To this purpose, the occurrence of sodium in ZDC was determined through sequential extraction with pure water, 1 mol/L NH_4Ac and 1 mol/L HCl as reported in previous literature [12], and the results were shown in Figure 7a. Clearly, the dominant sodium forms in ZDC are H_2O -soluble, NH_4Ac -soluble and HCl -soluble, which are volatile at high temperatures and tend to evolve into gas phase. Additionally, the sodium content in ZDC reaches 5.68 mg/g-coal, which is very high considering its extremely low ash content (3.6 wt.% on air-dried basis). Theoretically, the more sodium retained in ash, the less is released into gas phase, then the ash-related problems such as slagging, fouling and corrosion can be mitigated. The compositions of ashes were determined with XRF, and the results were listed in Table 4. As expected, the content of CaO and Na_2O decrease while those of SiO_2 and Al_2O_3 increase with rising co-firing ratios of ZDG. With the ash compositions and sodium occurrence in ZDC, the sodium retention (η_{Na}) in ash can be calculated with Equation (8).

$$\eta_{\text{Na}} = \frac{m_{\text{ash}} \times \varphi_{\text{Na-ash}}}{m_{\text{ZDC}} \times \varphi_{\text{Na-ZDC}} + m_{\text{ZDG}} \times \varphi_{\text{Na-ZDG}}} \times 100\% \quad (8)$$

where $\varphi_{\text{Na-ash}}$, $\varphi_{\text{Na-ZDC}}$ and $\varphi_{\text{Na-ZDG}}$ are the ash content in ash, ZDC and ZDG, respectively. The effect of co-firing on sodium retention was illustrated in Figure 7b. Clearly, η_{Na} monotonously rises with increasing ZDG ratios. Taking into account the varying ash compositions of ZDC and ZDG, it can be speculated that sodium silicates, sodium aluminates or sodium aluminosilicates are formed during co-firing thus facilitate the remaining of sodium in ashes. This speculation is highly probable despite that little Na-containing compounds are determined from their XRD patterns (Figure 5), which is possible due to their non-crystalline states or the concealment of other minerals (such as quartz) with high diffraction intensity. The result is consistent with the findings that silica and alumina effectively inhibited the release of sodium during combustion [9,47,48]. This corroborates that the co-firing effectively enhances the sodium retention, thus favoring the elimination of the ash-related problems.

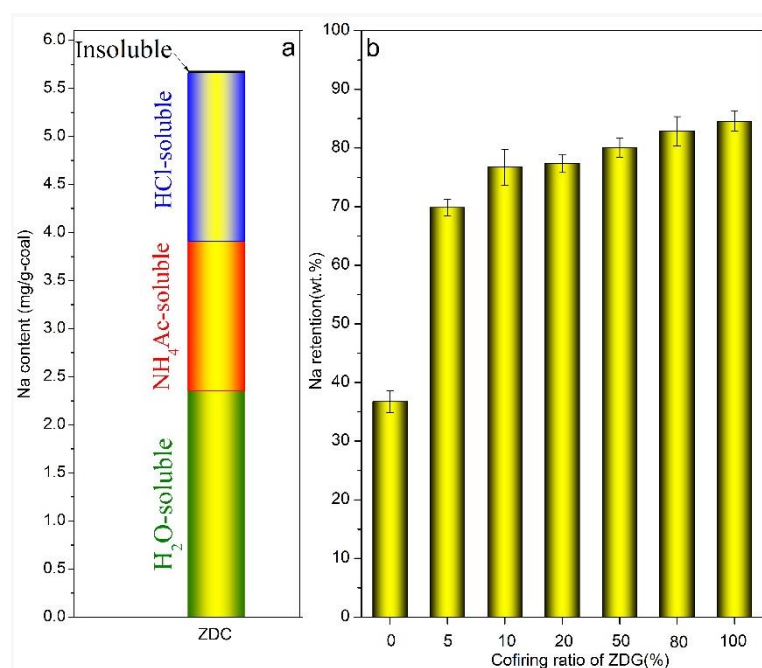


Figure 7. Sodium occurrence in ZDC (a) and Na retention during co-firing (b).

Table 4. Chemical compositions of the ashes.

Sample	Mass Fraction (%)										
	CaO	SiO ₂	Al ₂ O ₃	SO ₃	Na ₂ O	MgO	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	K ₂ O	Others
100ZDG	4.86	57.76	22.99	0.67	2.48	1.94	5.60	0.00	0.97	1.88	0.85
80ZDG20ZDC	5.39	56.83	22.68	0.93	2.62	2.26	5.92	0.24	0.96	1.82	0.35
50ZDG50ZDC	6.96	54.52	22.23	1.58	2.82	2.89	5.80	0.22	0.91	1.72	0.35
20ZDG80ZDC	12.28	46.19	19.93	3.98	3.70	5.12	5.96	0.20	0.85	1.38	0.41
10ZDG90ZDC	18.05	36.36	17.06	7.13	4.91	7.74	6.32	0.16	0.75	1.04	0.48
5ZDG95ZDC	24.20	25.78	13.70	11.23	6.02	10.73	6.24	0.11	0.64	0.76	0.59
100ZDC	38.71	5.66	7.31	15.32	8.35	15.81	7.24	0.03	0.36	0.13	1.08

3.3. Slagging and Fouling Propensity

The slagging and fouling indexes calculated according to Section 2.4 were presented in Figure 8. The judgement boundaries for the indexes are listed in Table 5. Clearly, the S_R of ZDC ash is only 8.39, inferring its high propensity of slagging. However, S_R of ZDG ash is up to 82.3, indicating its low viscosity and weak slagging tendency. The value of S_R gradually increases with the rising co-firing ratio of ZDG, and when the ratio is 50%, the viscosity reaches 77.7 and appears acceptable for practical operations [44]. The $R_{b/a}$ and R_s of ZDC ash reaches up to 5.27 and 2.90, both suggesting its severe slagging tendency. These parameters monotonously reduce as the co-firing ratio of ZDG increases, and when the ratio reaches 80% and 100%, it could reduce $R_{b/a}$ and R_s to the slight slagging zone. The F_u of ZDC ash is 2.21, revealing its moderate fouling tendency. By co-firing with 5% ZDG, the fouling index is reduced to 0.51, thus greatly lowering the ash-fouling probability. The H_m value linearly rises with co-firing ratios, and it should be kept at lower than 50% to avoid severe wearing of boilers. All these indexes collectively corroborate the efficacy of co-firing ZDG to reduce the ash-fouling and slagging tendencies under appropriate conditions.

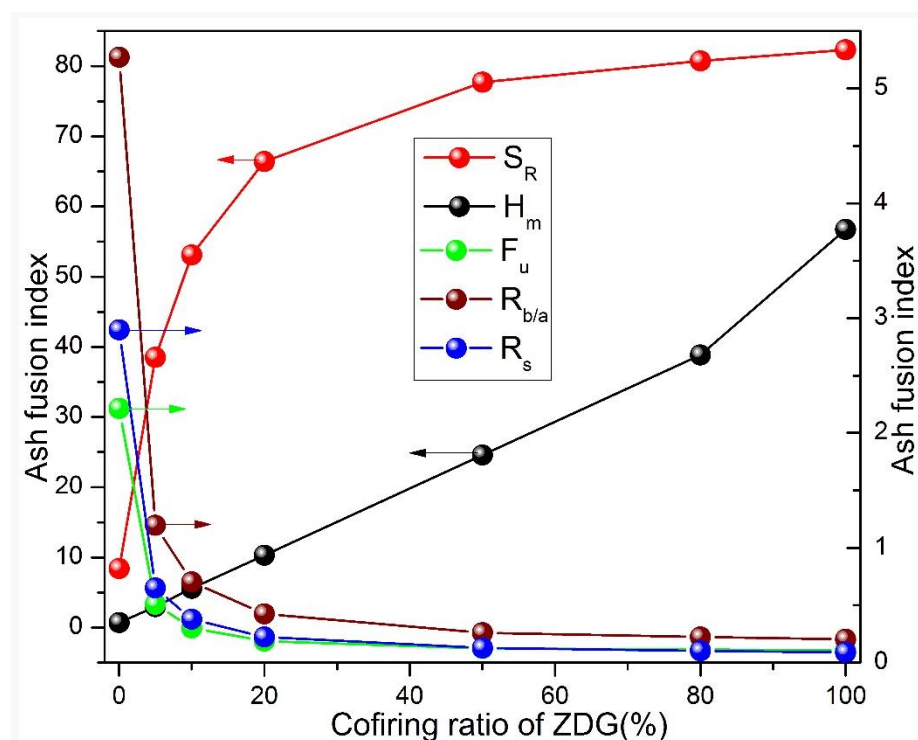
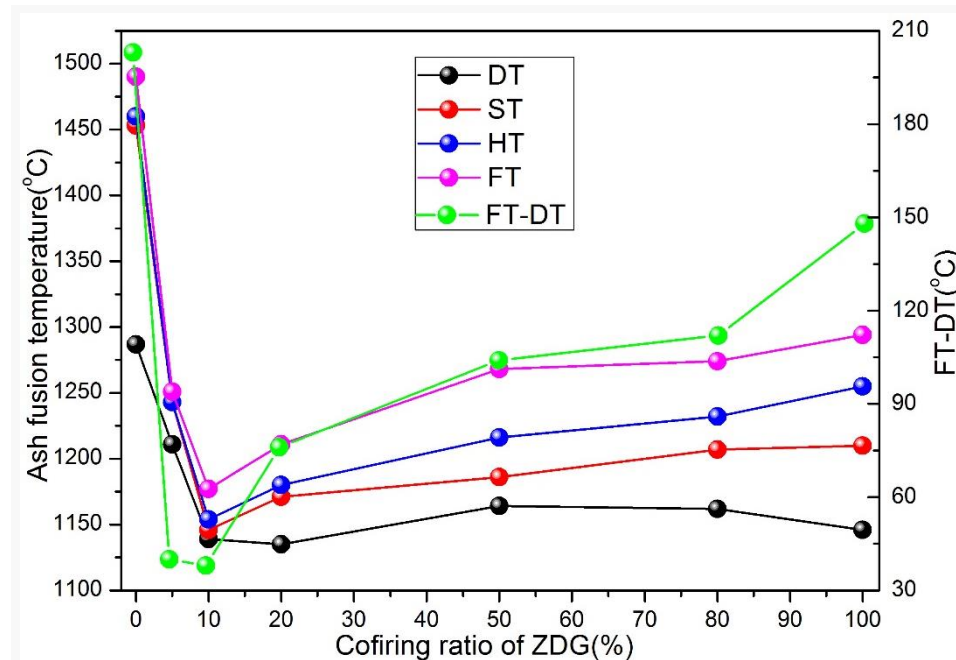
**Figure 8.** Effect of ZDG addition on fouling and slagging tendency of ash.

Table 5. Judgement boundaries for various indexes [8,44].

Discrimination Indexes	Slagging Judgement Boundaries		
	Light	Medium	Severe
S_R	>72	65–72	<65
$R_{b/a}$	<0.206	0.206–0.4	>0.4
R_s	<0.6	0.6–2.0	>2.6
F_u	<0.6	0.6–40	>40
H_m	<10%, mild wear	10–20%, medium wear	>20%, severe wear

3.4. Ash Melting Temperatures

The ash melting temperatures were determined to clarify the effect of co-firing on the melting behaviors (Figure 9). All the characteristic melting temperatures (including DT, ST, HT and FT) first decreases and then increases with the rising co-firing ratios of ZDG, reaching the minimum value at 10%. This result indicates that the ashes of 10ZDG90ZDC are more likely to deform, soften and flow at high temperatures than other co-firing samples. Surprisingly, the ZDC shows the highest ash melting temperatures among the samples, which is in distinct contrast with the predicted slagging and fouling tendency as previously discussed. This result is also discrepant with the production experience of thermal plants burning HSC. Unfortunately, the discrepancy cannot be clarified unambiguously currently, as the melting behavior is controlled by multiple factors such as temperature, atmosphere, ash composition and materials of heat transfer surface in boilers. Still, these results imply that the ash fusion temperatures are tunable by co-firing ZDC with ZDG, thus providing alternative means to reduce ash-related problems, and to realize the reduction and utilization of coal gangue concurrently.

**Figure 9.** Ash melting temperatures of the co-firing ashes.

4. Conclusions

To alleviate the ash-related problems, especially fouling and slagging, for burning HSC, as well as to realize resource utilization of coal gangues, this work performed co-firing tests of ZDC and ZDG and investigated the co-firing performance, combustion kinetics and sodium retention as well as slagging and fouling tendency of the ashes. The main results and conclusions are summarized below.

- (1) ZDC ignites more easily than ZDG due to its higher content of combustible substances. Co-firing ZDG does not hinder ignition but lowers the burning rate of ZDC. The comprehensive combustion index (S_N) gradually decreases with the reducing $(VM_{ad} + FC_{ad})/Ash_{ad}$. However, the burning rate increases at proper co-firing ratios (e.g., 10% or 20%) of ZDG.
- (2) Co-firing ZDC and ZDG follows the mechanism of a 3D diffusion model (cylinder symmetry) during non-isothermal combustion in TGA. The activation energy obtained from the mathematical fitting process with the model probably reflects the diffusion resistance of oxygen molecules to the carbon matrix of the fuels.
- (3) The enriched silica and alumina in ZDG can react with the calcium, magnesium and sodium in ZDC to form complex minerals. The sodium retention in ashes is remarkably enhanced. The varying indexes including S_R , $R_{b/a}$, R_s , H_m and F_u indicate the effectiveness of co-firing ZDG in reducing the propensity of ash-fouling and slagging.

These results corroborate the effectiveness of co-firing HSC and coal gangues to alleviate the ash-related problems; meanwhile, they shed light on the reduction and utilization of coal gangue.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su142416451/s1>.

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