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Flue Gas-Enhanced Water Leaching: AAEM Removal from Agricultural Organic Solid Waste and Fouling and Slagging Suppression during Its Combustion

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ABSTRACT: Alkali and alkaline earth metals (AAEMs) in agricultural organic solid waste (AOSW) contribute to the fouling and slagging during its combustion. In this study, a novel flue gas-enhanced water leaching (FG-WL) method using flue gas as the heat and CO_2 source was proposed for effective AAEM removal from AOSW before combustion. The removal rate of AAEMs by FG-WL was significantly superior to that by conventional water leaching (WL) under the same pretreatment conditions. Furthermore, FG-WL also obviously reduced the release of AAEMs, S, and Cl during AOSW combustion. The ash fusion temperatures of the FG-WL-treated AOSW was higher than that of WL. The fouling and slagging tendency of AOSW greatly decreased through FG-WL treatment. Thus, FG-WL is a simple and feasible method for AAEM removal from AOSW and suppressing fouling and slagging during its combustion. Besides, it also provides a new pathway for the resource utilization of power plant flue gas.
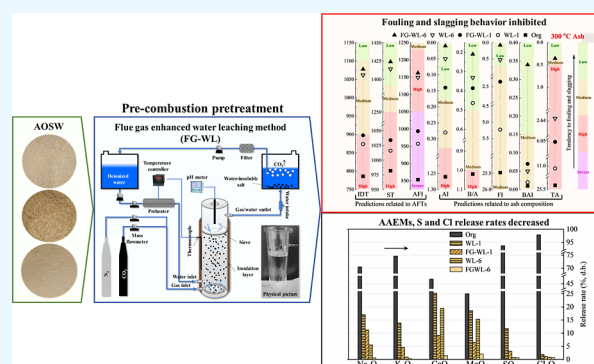
1. INTRODUCTION

The worldwide amount of agricultural organic solid waste (AOSW) generated annually is enormous.[1,2] One of its main uses is as fuel.[3] However, the high levels of alkali and alkaline earth metals (AAEMs) in AOSW are known to be responsible for severe fouling and slagging problems in boilers.[4,5]

Fouling and slagging problems are mitigated by various measures before, during, or after combustion. Precombustion pretreatment is to remove AAEMs in advance by leaching, and during combustion, controls use additives to reduce the proportion of AAEMs in ash to inhibit slagging.[6,7] Post-combustion, control methods generally involve periodic cleaning of the slag body with a slag removal device.[8] Among the measures, the leaching method is simple and effective in reducing the AAEM content in AOSW. This provides a fundamental solution to the problem of fouling and slagging in the combustion process and has broad utilization prospects. However, ordinary water leaching (WL) only works on metal compounds in the water-soluble state in AOSW and is unable to remove metal elements in the organic state, which are bound to carboxyl groups and inorganic metals in the water-insoluble state such as $CaCO_3$.[9] Leaching with conventional acids (such as HCl, HNO_3, etc.) is one way to solve the above problems.[10] However, high cost, corrosion of equipment, and acidic wastewater treatment make its practical application difficult.

Therefore, seeking an environmentally friendly and low-cost acid is an effective way to improve the removal efficiency of AAEMs from AOSW. Based on the principle that carbonic acid formed by CO_2 dissolved in water is effective in dissolving water-insoluble but acid-soluble AAEM compounds, this work proposed to enhance the AAEM removal from AOSW by WL using CO_2 from flue gas of a biomass-fried boiler, which is named the flue gas-enhanced WL (FG-WL) method. It is well known that carbonic acid decomposes rapidly in water without continuous CO_2 supply, so there is no acidic waste generated after the leaching. In addition, the high temperature of the flue gas can boost the chemical reaction and AAEM removal efficiency.[11] Besides the enhancement of AAEM removal, this method provides a novel approach to utilizing waste heat and CO_2 for biomass-fired boilers.

For AOSW, the existing form of AAEMs is the key factor to determine whether FG-WL is applicable and more efficient than WL.[12,13] The alkali metals of K and Na exist in similar
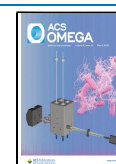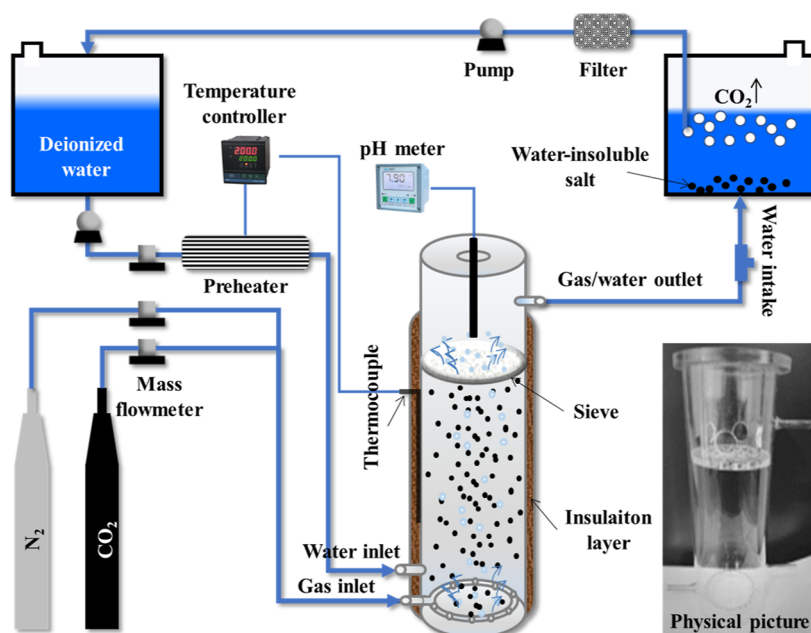
Figure 1. Semi-continuous leaching device and system.

forms, with the water-soluble state dominated by alkali metal salts and the water-insoluble state dominated by oxygen-containing functional groups of organic matter. For Ca in alkaline earth metals, the water-soluble state is relatively low and mainly present in lignin, and the water-insoluble state is mostly present in the organic state in the cell wall. For Mg, it exists mainly in chlorophyll in the water-insoluble organic state, and a small portion is a water-soluble salt.[14−17] So, it is reasonable to speculate that the removal of AAEMs from AOSW by WL is limited. However, the weak acid leaching of FG-WL can theoretically react with the weak bonds of the organic state of AAEMs in AOSW by ion exchange. It is foreseeable that FG-WL will be more capable than WL to dealkalize AOSW and inhibit fouling and slagging during its combustion. In addition, AAEMs in the organic state in AOSW largely release during combustion, which promote $PM_{2.5}$ generation. Thus, the FG-WL treatment should have a significant advantage than WL in terms of inhibiting fouling and slagging and PM release during AOSW combustion.

In order to verify the above theory, this work investigated FG-WL of typical AOSW at various temperatures and times. The effect of key operating parameters on AAEM removal efficiency was studied and compared in detail. Based on ash melting temperature and composition and its release during leached AOSW combustion, the mitigation effect of FG-WL on AOSW fouling and slagging problems was predicted in detail. This work not only confirms the efficiency and advantage of this FG-WL method but also provides support for the industrialization of the method.

2. MATERIALS AND METHODS

2.1. Materials. The wheat straw (WS), peanut shell (PS), and cotton straw (CS) used in this study were from Wuhan, China. These three AOSWs represent grain crop, oil crop, and cash crop wastes, respectively. According to the Chinese standards for preparation methods (GB/T 35820-2018), the samples were crushed and sieved to 0.2−0.4 mm and

subsequently vacuum-dried at 50 °C for 24 h to remove moisture prior to the experiment.

2.2. Leaching Experiments. The physical diagram of the leaching device and the system is shown in Figure 1. A 0.6 L semi-continuous leaching device was designed and constructed. For FG-WL experiment, 20 g of the sample was put into the device and leached by continuous injection of deionized water with a flow rate of 20 mL/min and simulated flue gas with a flow rate of 200 mL/min. The flue gas passes through a gas distribution tube at the bottom of the leaching device, creating a bubble stream that provides disturbing force for the leaching. The leached AOSW was filtered and vacuum-dried at 50 °C for 2 h. Under the same conditions, pure N_2 was used instead of flue gas for the WL experiment. Parallel experiments were conducted for both WL and FG-WL to confirm that the relative deviation was less than 6.5%.

The simulated flue gas is composed of 85% N_2 and 15% CO_2. The pH of the FG-WL leaching solution was determined to be between 5.1 and 5.4 at the experimental temperature. The abbreviations of the leached samples were named in the order of "leaching duration-leaching temperature", for example, 3−60 represented the samples leached for 3 h at 60 °C.

2.3. Ashing Experiments. Approximately 4.0 g of the sample was placed in a porcelain boat (60 × 90 mm) and then placed in a muffle furnace to produce low-temperature ash and high-temperature ash. The sample was first heated from room temperature to 200 °C at a heating rate of 5 °C/min, held for 90 min, and then heated up to the target temperature (300, or 1000 °C) at a heating rate of 3 °C/min.[18,19] Differently, the low-temperature ashes were prepared by being kept at 300 °C for 1.5 h, while the high-temperature ashes were kept at 1000 °C for 0.5 h.

2.4. Analytical Methods. The proximate analysis was performed using a muffle furnace according to GB/T 28731-2012. The ultimate analysis was performed on an elemental analyzer (Elementar, Vario Micro Cube, Germany). The AAEM contents were determined in the digestion filtrate by microwave plasma atomic emission spectrometry (MP-AES,

Table 1. Summary of Fouling and Slagging Indexes

indexes	Expression	range and criteria				reference
		low	medium	high	severe	
initial deformation temperature	IDT (°C)	>1100	900−1100	<900		4
sphere temperature	ST (°C)	>1390	1250−1390	<1250		23
ash fusibility index	AFI (°C) = 4 × IDT + HT/5	>1342	1232−1342	1052−1232	<1052	24
alkali index	$AI = \dfrac{ash\ \%(d.\ b.\ ) \times (K_2O + Na_2O)\%}{HHV(GJ/kg)}$	<0.17	0.17−0.34	>0.34		25, 26
basic to acidic compound ratio	$B/A = \dfrac{(Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5)\%}{(SiO_2 + TiO_2 + Al_2O_3)\%}$	<0.5	0.5−1.0	>1		27, 28
fouling index	$FI = B/A \times (K_2O + Na_2O)\%$	<0.6	0.6−40.0	>40.0		28
bed agglomeration index	$BAI = \dfrac{(Fe_2O_3)\%}{(K_2O + Na_2O)\%}$	>0.15		<0.15		29
total alkalis	$TA = (K_2O + Na_2O)\%$	<0.3	0.3−0.4	>0.4		30

Agilent, 4200, USA). The obtained ashes were stored in a desiccator and tested for chemical composition using an X-ray fluorescence spectrometer (XRF: EDAX, ESGLE III, USA). The ash fusion temperatures (AFTs) were determined by the ash melting point tester according to GB/T 30726-2014, including the initial deformation temperature (IDT), sphere temperature (ST), hemispherical temperature (HT), and fluid temperature (FT).

2.5. Data Analysis. The higher heating value (HHV, MJ/kg) of the samples was calculated by the formula as eq 1[20]

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \tag{1}$$

where C, H, S, O, and N are their contents of the sample (on dry ash-free basis, %) and A is the ash contents of the sample (on dry basis, %).

The removal rate of total ashes (R_A, %) was calculated through formula 2[21,22]

$$\text{Removal rate of total ashes (\%)} = \left(1 - \frac{A_{leached}}{A_{org}}\right) \times 100\% \tag{2}$$

where A_{org} and $A_{leached}$ are the ash contents of the sample (wt %, d.b.).

The removal rates of AAEMs (R_{Na}, R_K, R_{Ca}, and R_{Mg}, respectively) were calculated by comparing K^+, Na^+, Ca^{2+}, and Mg^{2+} in the leached sample to these in the raw sample, as defined by formula 3.[21,22]

$$\text{Removal rate of AAEMs (\%)}$$
$$= \left(1 - \frac{AAEMs_{leached}}{AAEMs_{org}}\right) \times 100\% \tag{3}$$

where $AAEMs_{org}$ and $AAEMs_{leached}$ are the AAEM contents of the sample (wt %, d.b.).

The release rates of AAEMs, S, and Cl were calculated from their contents in low-temperature and high-temperature ashes, as shown in formula 4.

$$\text{Release rate (\%)} = \left(1 - \frac{A_{1000\ °C} \times content_{1000\ °C}}{A_{300\ °C} \times content_{300\ °C}}\right)$$
$$\times 100\% \tag{4}$$

where $A_{1000\ °C}$ and $A_{300\ °C}$ represent the ash content (wt %, d.b.), where $content_{1000\ °C}$ and $content_{300\ °C}$ represent the oxide content of AAEMs, S, or Cl in high-temperature and low-temperature ashes (wt %, d.b.).

2.6. Fouling and Slagging Prediction. The composition and AFTs of the low-temperature ash were used to predict their fouling and slagging tendency during combustion through various evaluation indicators, as shown in Table 1.

3. RESULTS AND DISCUSSION

3.1. Basic Characteristics of Leached Samples. In this section, the effects of FG-WL and WL on the basic characteristics of the samples are studied comparatively. Table 2 illustrates the proximate and ultimate analysis results of the original and leached samples. For both C and H contents, increasing the temperature or extending the leaching duration contributed to the increase in C and H contents for both FG-WL and WL. Under the same leaching conditions, the differences between FG-WL and WL for C and H contents were not significant. For S and O, their contents were reduced from 0.21 to 0.68 wt % and 41.91−46.19 to 0.03−0.20 wt % and 38.45−41.83 wt % after FG-WL and WL, respectively. This is also reflected in the fact that the HHV of the leached AOSW is all higher than that of the original samples. In particular, the leached PS has HHV values close to those of lignite (23−30 MJ/kg).[31]

The leaching of O-containing hydrophilic organic small molecules such as sugars, organic acids, lipids, and S-containing substances from AOSW increases the percentage of lignocellulose, leading to an increase in C and H content and a decrease in O and S content.[32,33] This process inevitably results in the partial loss of neutral detergent solutes from the sample.[34] Figure 2 shows the mass yields of the leached AOSW on a dry and ash-free basis. Around 15−25% of organics are removed by WL and FG-WL. The yields of FG-WL samples are all slightly lower than those of WL, indicating that FG-WL is more favorable for the removal of organic matter.

3.2. Ash Removal. The R_A values of ASOWs leached by WL and FG-WL are shown in Figure 3. All the three AOSWs have R_A above 40%, and FG-WL is higher than WL regardless of the conditions. The ash content in the original WS was 9.3 wt %, which was much higher than that of PS of 3.1 wt % and CS of 3.6 wt %. However, the R_A value of WS was the lowest of the three AOSWs under all conditions of WL or FG-WL. After FG-WL at 20 °C for 6 h, the R_A value of WS was only 55.6%,

Table 2. Proximate Analysis, Ultimate Analysis, and HHV of Samples

|	leaching parameters		proximate analysis (wt %, d.b.)			ultimate analysis (wt %, d.a.f.)					
sample	duration (h)	temperature (°C)	VM	FC[a]	A	C	H	O[a]	N	S	HHV (MJ/kg)
					WS						
original			76.25	14.46	9.29	46.12	6.14	46.19	0.87	0.68	18.42
WL	1	20	83.78	11.05	5.17	50.02	6.75	42.36	0.72	0.15	20.97
	1	40	83.02	11.86	5.12	49.83	6.83	42.35	0.85	0.14	20.95
	1	60	84.04	10.90	5.06	49.98	6.80	42.20	0.92	0.11	20.98
	3	20	84.97	10.30	4.73	50.57	6.81	41.74	0.79	0.10	21.26
	6	20	86.05	9.47	4.47	50.59	6.78	41.83	0.71	0.09	21.22
FG-WL	1	20	83.30	11.96	4.74	50.02	6.32	42.81	0.64	0.20	20.41
	1	40	84.03	11.28	4.69	50.07	6.62	42.44	0.67	0.20	20.80
	1	60	83.94	11.35	4.71	49.54	6.83	42.60	0.83	0.19	20.85
	3	20	86.14	9.14	4.72	49.41	6.69	42.89	0.85	0.16	20.60
	6	20	85.81	10.07	4.12	50.74	6.60	41.61	0.88	0.16	21.11
					PS						
original			77.24	19.66	3.10	50.67	5.22	42.81	0.80	0.49	19.39
WL	1	20	79.82	18.53	1.65	54.22	6.49	38.22	1.00	0.07	22.59
	1	40	80.33	18.05	1.62	53.96	6.53	38.36	1.09	0.05	22.52
	1	60	79.91	18.59	1.50	53.88	6.51	38.52	1.04	0.05	22.45
	3	20	79.53	19.00	1.47	53.68	6.57	38.86	0.84	0.06	22.42
	6	20	80.14	18.46	1.41	53.88	6.40	38.45	1.22	0.05	22.33
FG-WL	1	20	80.76	17.72	1.52	52.99	6.43	39.40	1.04	0.14	21.97
	1	40	79.43	19.11	1.45	52.16	6.62	40.13	0.96	0.13	21.83
	1	60	79.83	18.77	1.40	52.02	6.49	40.14	1.20	0.14	21.63
	3	20	79.77	18.89	1.34	51.75	6.48	40.46	1.17	0.13	21.49
	6	20	81.57	17.44	1.00	52.28	6.51	39.96	1.14	0.12	21.77
					CS						
original			79.18	17.18	3.64	50.43	6.36	41.91	1.09	0.21	1.00
WL	1	20	84.93	13.79	1.28	50.98	6.60	41.63	0.75	0.04	1.03
	1	40	86.13	12.65	1.21	51.25	6.71	41.29	0.70	0.04	1.04
	1	60	86.25	12.63	1.12	51.12	6.73	41.36	0.76	0.03	1.04
	3	20	85.68	13.23	1.09	51.01	6.75	41.45	0.76	0.03	1.04
	6	20	86.14	12.90	0.96	51.68	6.77	40.77	0.74	0.03	1.05
FG-WL	1	20	86.24	12.62	1.14	49.99	6.61	42.59	0.71	0.09	1.01
	1	40	85.23	13.68	1.09	50.67	6.48	42.08	0.66	0.10	1.01
	1	60	85.92	13.07	1.01	51.09	6.66	41.34	0.80	0.11	1.03
	3	20	85.96	13.14	0.90	50.31	6.61	42.33	0.67	0.09	1.01
	6	20	87.48	11.97	0.56	50.78	6.59	41.99	0.55	0.09	1.02
				AAEM content (mg/g AOSW, d.b.)							
original		Na		K			Ca			Mg	
	WS	3.56		26.61			4.56			0.89	
	PS	0.56		13.31			4.62			2.70	
	CS	2.17		18.67			3.44			1.19	

[a]Calculated by difference.
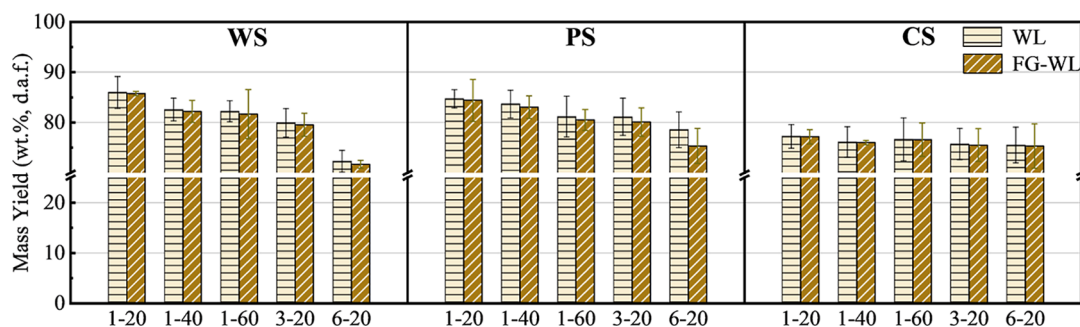
Figure 2. Mass yield of FG-WL and WL.

while that of PS and CS was 67.8 and 84.7%, respectively. This indicates that different AOSWs have large differences in the

ease of ash removal, and the order of deashing from easy to difficult is CS > PS > WS. The ability of ash removal is
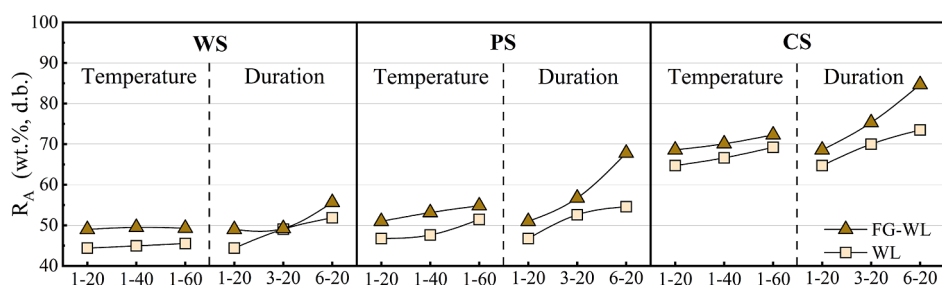
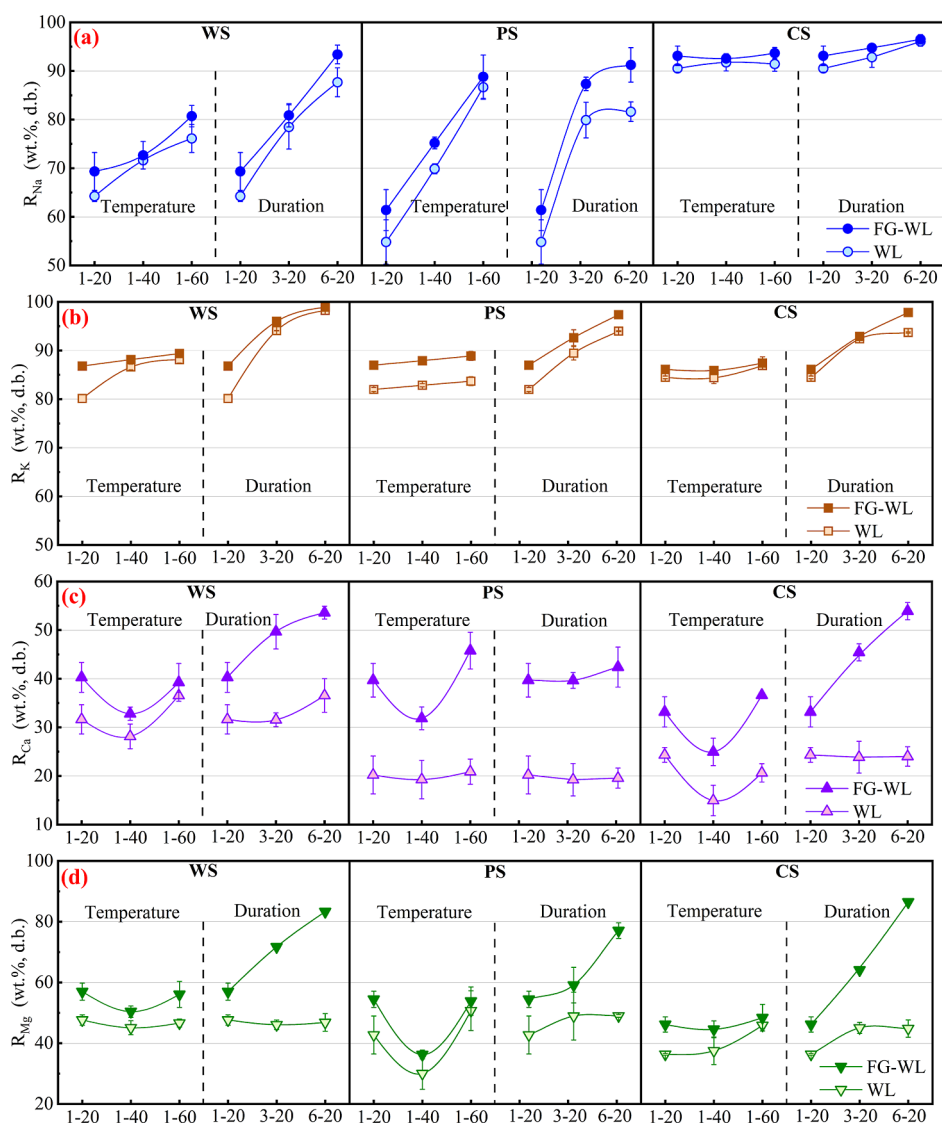**Figure 3.** Ash removal rate of FG-WL and WL.

Figure 4. Effect of leaching temperature and duration on the removal of AAEMs. (a) Removal rate of Na, (b) removal rate of K, (c) removal rate of Ca, and (d) removal rate of Mg.

influenced by many factors such as hydrophilicity, pore structure, AAEM content, and existence form of raw materials, which will be studied in detail in our next work.

R_A is influenced by both the increase in temperature and duration. The R_A value of the three AOSWs increased relatively slowly with increasing temperature (from 20 to 60 °C) during the 1 h leach. The R_A value of FG-WL is higher by 3.0−5.5% than that of WL. At 20 °C, both leaching methods produced a more pronounced increase in R_A with increasing

leaching duration from 1 h to 6 h. The R_A value of FG-WL was 0.2−13.2% higher than that of WL. In addition, the R_A enhancement of WL tended to level off with the increase of leaching duration, while FG-WL showed a rapid increasing trend, especially under long leaching duration. As processing durations increase, the advantages of FG-WL become more apparent.

3.3. AAEM Removal. The AAEM removal of different AOSWs vary greatly due to their properties. In this section, the
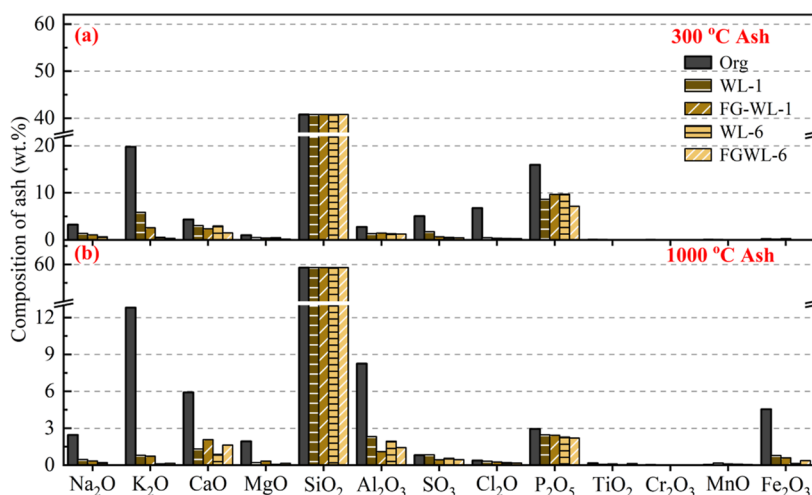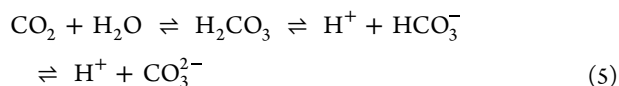
Figure 5. Composition of ashes. (a) Low-temperature ash and (b) high-temperature ash.
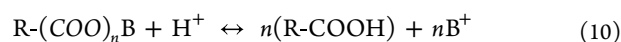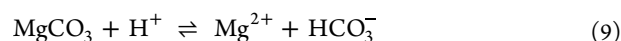
two key parameters of leaching temperature and duration were investigated in detail on the removal pattern of AAEMs from three feedstocks. The macroscopic laws were obtained by comparing the two leaching methods, and it can provide insight into wider AOSWs.

3.3.1. Leaching Temperature. The removal rates of alkali metals (Na and K) are shown in Figure 4a,b. The removal of alkali metals was more than 50%. More than half of the alkali metals in AOSW are present as inorganic salts in the water-soluble state (such as chloride, nitrate, carbonate, sulfate, phosphate, etc.). Increasing the water temperature from 20 to 60 °C tends to increase the solubility of these salts, which facilitates the removal of alkali metal salts. The regularities of R_{Na} and R_K are similar for the two leaching methods. However, the removal by FG-WL is always higher than WL in all cases. Particularly, FG-WL achieves a R_K value at low temperatures, while WL requires a higher temperature to achieve this value as shown in Figure 4b. It was found that ion exchange of hydrogen ions (H^+) is well suited to replacing organic minerals in AOSW.[35] The higher R_{Na} and R_K obtained by FG-WL is due to the pH of the leaching solution <5.5, which facilitates the removal of organic alkali metals ($-COONa$ and $-COOK$). The ion-exchange reactions are shown in eqs 5−7.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$\rightleftharpoons H^+ + CO_3^{2-} \tag{5}$$

$$R\text{-}COONa + H^+ \leftrightarrow R\text{-}COOH + Na^+ \tag{6}$$

$$R\text{-}COOK + H^+ \leftrightarrow R\text{-}COOH + K^+ \tag{7}$$

The removal rates of alkaline earth metals (Ca and Mg) are shown in Figure 4c,d. In terms of WL, R_{Ca} and R_{Mg} ranged between 14.9−36.5 and 30.0−50.7%, respectively. However, for FG-WL, R_{Ca} and R_{Mg} were elevated to 24.9−48.8 and 36.2−56.9%, respectively. There is no doubt that FG-WL has a superior ability to enhance the alkaline earth metal removal. The main reasons are as follows. First, the weakly acidic environment provided by FG-WL facilitates the dissolution of alkaline earth metal carbonates, as shown in formulas 4 and 5. Second, the acidic environment is also favorable for the removal of ion-exchangeable alkaline earth metals ($-COO\text{-}CaOOC-$ and $-COOMgOOC-$). Particularly for AOSW, Ca and Mg are mainly in an organic ion-exchangeable form,

accounting for about 60 and 50%, respectively.[16] FG-WL facilitates alkaline earth metal removal as shown in eqs 8−10.

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \tag{8}$$

$$MgCO_3 + H^+ \rightleftharpoons Mg^{2+} + HCO_3^- \tag{9}$$

$$R\text{-}(COO)_n B + H^+ \leftrightarrow n(R\text{-}COOH) + nB^+ \tag{10}$$

It is noteworthy that the removal rate of alkaline earth metals by FG-WL first decreases and then increases as the temperature increases. The increase in temperature promotes the dissolution of inorganic salts of alkaline earth metals (sulfates of Ca and Mg, phosphates, nitrates, chlorides, etc.) during leaching. However, more importantly, the high temperature inhibits the dissolution of CO_2 and carbonate in water. A complex balance exists between the effects of temperature on alkaline earth metal removal from FG-WL, which needs to be studied in more depth.[36]

Overall, the increase in temperature favors the removal of Na and K, but the effect on Ca and Mg removal is complex. FG-WL was able to remove more AAEMs than WL at the same temperature.

3.3.2. Leaching Duration. For alkali metals, as shown in Figure 4a,b. After 1−6 h of WL at 20 °C, R_K is maintained at 80.1−98.2% and R_{Na} at 54.8−96.1%. For FG-WL, the trends of R_{Na} and R_K were basically the same but higher than those of WL as the leaching duration variation; especially in R_{Na}, the PS leached by FG-WL for 6 h was 9.6% higher than that by WL.

For alkaline earth metals, as illustrated in Figure 4c,d. FG-WL was always superior to WL with the maximum difference for CS by 6 h. WL is only slightly affected by duration, and the maximum effect is on the R_{Mg} of CS, which increases from 36.3% at 1 h to 44.8% at 6 h. In contrast, the duration had a significant effect for FG-WL on R_{Mg} of CS, which increased from 46.2% at 1 h to 86.5% at 6 h. This is because WL only removes water-soluble alkaline earth metals,[7,37] and this process is fast, e.g., 1 h is sufficient. However, organic alkaline earth metals may be dissolved relatively slowly in carbonic acid and require more time. Besides, FG-WL can also be interpreted as two stages in sequence. The first stage is water-soluble metal removal stage and the second stage is acid-soluble metal removal stage.
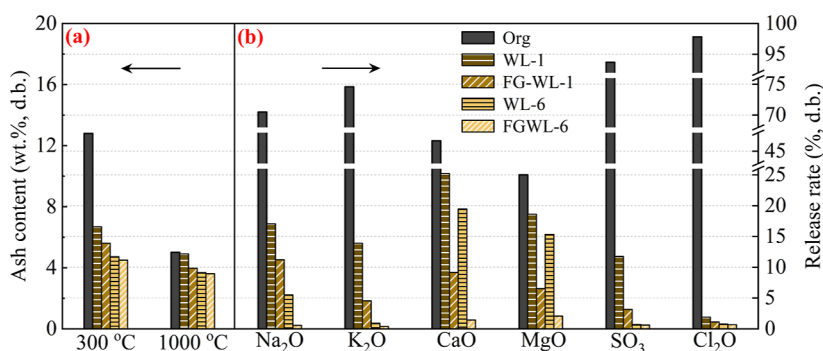
Figure 6. Content and release of ashes. (a) Ash content of low-/high-temperature ash and (b) release rates of the main minerals.
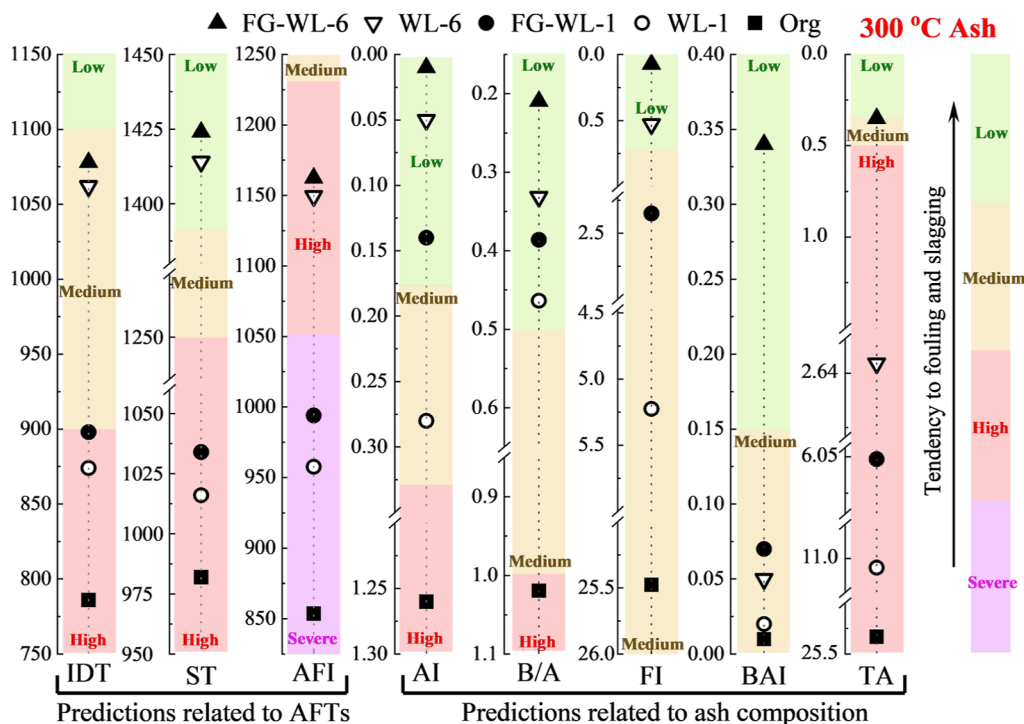

Figure 7. Prediction of fouling and slagging behavior during original and leached WS.

3.4. Characterization of Ash and Prediction of Fouling and Slagging Behavior.

Since WS has the highest ash and AAEM contents among the three AOSW, it is reasonable to speculate that WS has the most severe fouling and slagging tendency. Therefore, detailed characterization of WS ash and prediction of fouling and slagging during original and leached WS combustion were conducted.

3.4.1. Chemical Composition of Ash. Slagging and fouling are directly influenced by the chemical composition of AOSW ash.[38] Based on the fact that SiO_2 is insoluble in water and weak acids, the absolute contents of each metal oxide in low-temperature ash and high-temperature ash were obtained using the SiO_2 content as a reference, as shown in Figure 5a,b.

The low-temperature ash was prepared at 300 °C for avoiding the volatilization of AAEMs at elevated temperatures, so the chemical composition of the low-temperature ash is considered to be the actual ash composition of the samples.[39] In the low-temperature ash, the K_2O and CaO contents of the original samples were as high as 19.7 and 4.3 wt %, respectively. For FG-WL-1/6, K_2O was reduced to 2.6 and 0.3 wt %, and CaO was reduced to 2.4 and 1.5 wt %,

respectively. While in WL-1/6, K_2O was still 5.8 and 0.6 wt %, and CaO was still 3.1 and 3.0 wt %, respectively. The AAEM content in the ash from FG-WL-treated samples was lower than that of the corresponding WL-treated samples. Additionally, FG-WL is also more effective for S and Cl removal compared to WL. The SO_3 and Cl_2O contents were 0.67 and 0.35 wt % for FG-WL-1, respectively, while they were 1.75 and 0.48 wt % for WL-1.

The high-temperature ash prepared at 1000 °C is considered to be the actual combustion ash. The composition of high-temperature ash differs significantly from low-temperature ash. First, K and Na readily migrate into the gas phase at high temperature. The proportion of alkali metals in high-temperature ash decreases. The percentage of K_2O decreased from 19.7 wt % of the original sample to 12.8 wt %. Second, the enrichment of high melting point metals such as Si, Al, and Fe in the ash appears. For example, the percentage of SiO_2 increased from 40.8 to 59.7 wt %. It is noteworthy that the Ca and Mg contents of the FG-WL-treated sample ash are higher than those of the corresponding WL-treated sample ash. This may be due to that the relatively high proportions of Si

and Al compounds, such as aluminosilicate in the FG-WL-treated sample ash, react with Ca and Mg and suppress their migration to the gas phase.

3.4.2. Release of AAEMs from Ash. Figure 6a shows the ash contents of samples measured by low-temperature ashing and high-temperature ashing. It is notable that the difference of the ash content for the original WS is 7.79 wt %, indicating that 60.9% of ash is released during its combustion. The ash release for the FG-WL- and WL-treated WS is much less, as shown in the Figure 6a. The release rates of the main minerals of WS were calculated by formula 4 and are shown in Figure 6b. It is evident that more than 70.5% of Na_2O, 74.6% of K_2O, 46.7% of CaO, and 25.0% of MgO were released during the original WS combustion. Aerosols containing AAEMs adhere to the inner surface of the furnace and cause fouling and slagging.[38] Moreover, as much as 93.7% SO_3 and 97.8% Cl_2O were also released during the original WS combustion, which can also cause serious corrosion of the boiler.[38,40]

WL mitigated the release of AAEMs to some degree. The release of Na_2O and K_2O was reduced to 17.0 and 13.9% by WL-1, respectively. Compared with WL-1, FG-WL-1 further reduced the release of Na_2O and K_2O to 11.2 and 4.6% and CaO and MgO to 9.2 and 6.5%. The AAEMs in the organic state in AOSW is largely released during combustion.[41] As FG-WL removes much organic AAEMs, the release of AAEMs during FG-WL-treated AOSW combustion is lower than that of WL. In addition, it was found that the release of organic AAEMs is directly related to PM generation during biomass combustion; it is thus expected that the PM generation of AOSW combustion is to be inhibited by FG-WL.[42] As for the control of S and Cl release, FG-WL is also more effective than WL.

3.4.3. Prediction of Slagging and Fouling Behaviors. The fouling and slagging tendency was classified as severe, high, medium, and low levels based on methods such as phase equilibrium and correlation analysis.[43] The specific classification range and criteria are shown in Table 1. Figure 7 and Table 3 show the AFTs of the low-temperature ash and various predictions of the fouling and slagging tendency.

Table 3. Ash Fusion Temperatures

AFTs	org	WL-1	FG-WL-1	WL-6	FG-WL-6
IDT	786	874	898	1062	1078
ST	982	1016	1034	1414	1424
HT	1124	1292	1378	>1500	>1500
FT	1224	1384	1424	>1500	>1500

All the four characteristic temperatures of the original WS ash were lower compared to the leached WS ashes. The AFTs of leached WS were raised, and the risk level of fouling and slagging gradually decreased to medium or low levels. This trend is more pronounced with longer leaching durations. FG-WL-1 and WL-1 have IDT of 898 and 874 °C, respectively, while FG-WL-6 and WL-6 have IDT of 1062 and 1078 °C, respectively. FG-WL-6 and WL-6 even reached ST of 1424 and 1414 °C, respectively. Furthermore, the melting point of the ash from the FG-WL-treated sample are always higher than that from the corresponding WL-treated sample.

It is evident that the ash composition and AFTs are closely related.[23] To further improve the accuracy of prediction, more appropriate predictions are carried out from the perspective of ash composition, as shown in Figure 7. Based on the

composition of the ash, the original samples have a high or medium tendency for fouling and slagging. After 1 h of leaching, the AI index showed that FG-WL-1 enters the low-tendency range from the high-tendency range, whereas WL-1 was in the medium tendency range; the BAI index also indicated that FG-WL-1 has a lower value than WL-1. After 6 h, the FG-WL-treated AOSW was in the low-tendency range, while WL failed to overcome the interval of severe or moderate tendency in the BAI and TA indices. This shows that FG-WL is more effective than WL at inhibiting fouling and slagging during AOSW combustion.

4. CONCLUSIONS

This work proposed a novel FG-WL method for effective AAEM removal from AOSW before combustion. The removal rate of AAEMs by FG-WL was significantly superior to that by conventional WL. The release of AAEMs, S, and Cl during AOSW combustion was obviously suppressed. The AFTs of the FG-WL-treated AOSW increased, and their fouling and slagging tendency during combustion greatly decreased. Thus, FG-WL is a simple and feasible method for AAEM removal from AOSW and suppressing fouling and slagging during its combustion. Besides, it also provides a new pathway for the resource utilization of power plant flue gas.

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Notes

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