A novel CO$_2$-water leaching method for AAEM removal from coal: Suppression of PM formation and release during Zhundong coal combustion

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**ABSTRACT**

Zhundong coalfield is one of the core coalfields in Xinjiang, China. Due to its high alkali and alkaline earth metal (AAEM) contents, large amounts of PM were released during Zhundong coal combustion, causing serious environmental pollution. In this paper, a novel CO$_2$-water leaching method was proposed to suppress the PM formation and release during Zhundong coal combustion. The results showed the CO$_2$-water leaching effectively removed water insoluble minerals from coal, such as Na, Ca, Mg, Cl and S, and significantly reduced the PM formation and release during the Zhundong coal combustion, especially for submicron particle formation and release. The releases of PM$_{1}$, PM$_{2.5}$, PM$_{10}$ were reduced by 29.09%, 22.68% and 18.48%, respectively. The detailed characterizations showed that the significant removal of the easily vaporized elements in the coal by CO$_2$-water leaching, such as Na, Ca, Mg, S and Cl, was an main factor for the suppression of PM formation and release. Besides, after CO$_2$-water leaching, the combustion characteristics of Zhundong coal were promoted. Thus, the CO$_2$-water leaching was a feasible method to inhibit the formation and release of PM during Zhundong coal combustion. Furthermore, since the flue gas from coal-fired power plant can be used as a source of CO$_2$, the CO$_2$-water leaching method provided a new way for the efficient utilization of the coal-fired flue gas.

1. Introduction

Zhundong coalfield in Xinjiang province of China is the largest intact coalfield in the world and accounts for 7.2% of Chinese coal reserves [1,2]. The efficient and clean conversion and utilization of Zhundong coal is of great significance. However, the special forming history and geographical environment caused rather high contents of alkali and alkaline earth metal (AAEM) in Zhundong coal. One of the serious problems caused by the high AAEM content in Zhundong coal was the formation and release of particulate matter (PM) during its combustion.

It’s well known that the formation of the submicron particle during the coal combustion is the condensation and agglomeration of easily vaporized elements, such as Na, Ca and Mg etc [3,4]. It was found that the Zhundong coal produced about 3.5 and 5.1 times of ultrafine particulates as much as common lignite and bituminous coals, respectively [5]. It was also found that the proportion of fine particles from combustion of high alkali coal was significantly higher than that of the conventional coal [6-8]. Gao et al. [9] studied the formation of ultrafine particles during Zhundong coal combustion on downward Hencken flat-flame burner. It was speculated that the precursor of fine particles is composed of Na$_2$SiO$_3$. Li et al. [10] analyzed the fine particles produced by combustion of Zhundong coal in a 25kw down-fired furnace and found that sodium sulfate was the main component of the particle with the size below 0.4 μm. Li et al. [5] also found the main vaporizable elements in ultrafine particles of Zhundong coal include Na, S, K, Ca, Mg, Cl and F, and the main components of submicron particles are Na and Ca sulfate and aluminosilicate. So, the previous research found that easily vaporized elements in coal, such as Na, Ca and K, play an important role for the fine particle formation during the coal combustion.

A lot of research has been done for suppressing the PM formation and release during coal combustion, which can be generally classified as: 1. Pre-combustion control, which is to reduce the mineral content in coal before combustion, such as water leaching [11,12]; 2. Combustion control, which
is to optimize the combustion conditions, or use mixed coal combustion and additives [13–17]; 3. Control after combustion, which is removing particle from flue gas by equipment such as bag filter and electrostatic precipitator [18]. Coal blending has been used to suppress this issue in coal-fired power plant. But it is confined by its low economy. Kaolin was found to be a good additive to capture AAEMs during coal combustion [8]. However, there are some issues, such as high cost and calorific value decline caused by the kaolin addition, limited its application for Zhundong coal combustion [13]. Water leaching is one of the feasible methods for suppressing the PM formation and release during coal combustion. However, water leaching can just remove the water soluble minerals in the coal, and the organically-bound mineral and water-insoluble inorganic minerals, such as CaCO₃ and MgCO₃, cannot be removed. Van Eyk et al. [19,20] found that about 100% of organic sodium and 67% of water-soluble sodium in coal were released during the char combustion and ash formation stage. Gao et al. [21] found that organically-bound Mg and Ca play dominant roles in PM₁₀ emission. So the effect of organically-bound minerals on the PM formation during the coal combustion should not be ignored.

In our previous work, a novel CO₂-water leaching method was proposed to remove AAEM from Zhundong coal to suppress the fouling and slagging issues during Zhundong coal combustion. The CO₂ dissolved in water, formed carbonic acid solution, which dissolved and removed a large percentage of organically-bound minerals and water-insoluble inorganic minerals in coal, such as carboxylate AAEM and carbonate Ca/Mg. The fusion temperature of the CO₂-water leached coal ash increased significantly, and the fouling and slagging issues of Zhundong coal combustion were then suppressed significantly. Furthermore, the flue gas from coal-fired power plant can be used as the source of CO₂, which provides a new way for the efficient utilization of the coal-fired flue gas.

The easily vaporized elements in coal, such as Na, Ca and K, play an important role for the fine particle formation during the coal combustion, and such elements can be removed significantly by the CO₂-water leaching, as discussed above. So the CO₂-water leaching may also be an effective way for suppressing PM formation during the Zhundong coal combustion, however, it was not studied and confirmed. Thus, this work systematically studied the effect of CO₂-water leaching on the formation, composition, particle size distribution of PM released during Zhundong coal combustion. The combustion behavior of the leached coals was also investigated. The feasibility of the CO₂-water leaching for suppressing the PM formation and release during Zhundong coal combustion was confirmed.

2. Experimental

2.1. Samples

Three typical Zhundong coals, Wucaiwan coal (WCW), Erkuang coal (EK) and Wanxianggaolv coal (WXGL), were used for the study. After dried under 105 °C for 5 h, the coals were milled and sieved to <150 mesh (100 μm). The proximate and ultimate analysis of the coal samples were conducted according to Chinese coal standard (CG/T212-2008) and shown in Table 1. The compositions of the raw coal ashes, obtained by low temperature ashing at 350 °C were shown in Table 2.

2.2. CO₂-water leaching

Zhundong coal and water were mixed in a Monteggia washing bottle with mass ratio of 1/50. CO₂ gas flow was set to 200 ml/min with flowmeter to keep the solution saturated with CO₂. The mixture was stirring for 24 h at room temperature, and then separated by Buchner funnel with suction filtration. The obtained coal was dried at 105 °C for 10 h. For comparison purpose, water leaching experiment under same conditions without CO₂ flow was also conducted. The specific steps were already described in our previous work [22,23]. The parallel
experiments were conducted for some runs and confirmed the relative deviations were smaller than 7%. Besides, it was also found that less than 5% of the organics was removed from coal by leaching.

2.3. Chemical sequential extraction

Chemical sequential extraction was conducted to investigate the existing form of Na in the three raw coals. The Zhundong raw coals were leached by deionized water, 1.0 mol/L NH₄Ac, 1.0 mol/L HCl with mass ratio of 1/50 for 24 h at 20 °C in turn. After acid leaching, the coal was washed by deionized water until the pH of leached water turn to neutral. The Na was divided into four forms by this method, which was water-soluble Na, NH₄Ac-soluble Na, HCl-soluble Na and insoluble Na.

2.4. Ashing experiments

In order to avoid vaporization and release of mineral elements in coal, low temperature (350 °C) ashing was conducted. The raw and leached coals in a porcelain boat (60 × 90 mm) were, placed in a muffle furnace. To ensure the complete combustion of coal samples, the thickness of coal in porcelain boat was kept less than 0.15 g/cm². The heating procedure was as follow: 1. room temperature to 300 °C with heating rate of 5 °C/min, heat preservation was 40 min; 2. 300 °C to 350 °C with heating rate of 5 °C/min, held until weight constant. The obtained coal ash was kept in a desiccator for later test.

2.5. Combustion experiments

The system of drop tube furnace (DTF, Fig. 1) includes five parts: the coal feeder system, gas distribution system, combustion system, sample collection system and auxiliary system. The specific parameters can be found in our previous study [7,24–26]. The powder feeding rate was kept at 0.3 g/min and the operating temperature was set at 1300 °C. In gas distribution system, air combustion atmosphere (O₂/N₂ = 21/79) was used and the gas flow rate was 10 L/min. The combustion system consists of two-stage burner. The inner burner carries a primary wind to blow the powder into the furnace. The external burner supplements the secondary air to ensure complete combustion of coal. The reactor was made of corundum tube material with a length of 2 m and an inner diameter of 56 mm. As for sample collection, the ash went through the bottom sampling tube, and then sequentially entered the cyclone and low pressure impactor (LPI). The cyclone was used to separate and collect different size of ash particulates.

The composition of coal ashes were analyzed by X-ray fluorescence (XRF, Panalytical BV, Zetium). X-ray diffractometer (XRD, Panalytical BV, Empyrean) was used to identify the mineral phases in ashes.

![Fig. 2. Existing form and proportion of Na in raw coals.](image)

2.6. Thermogravimetric experiments

The combustion behaviors of the raw coals and leached coals were characterized by a thermogravimetric analyzer (Pyris1 TGA, PerkinElmer). The sample was heated up to 900 °C from room temperature with the heating rate of 10 K/min by using air as carrier gas.

3. Results and discussion

3.1. Mineral removal efficiency and coal ash characteristics

3.1.1. Existing form of AAEM

The AAEM with different existing form has different vaporization characteristic during coal combustion and gasification [27,28]. Below 1000 °C, the release of the AAEM was mainly in the form of atomic, hydroxide, oxide, chloride, etc. Above 1000 °C, they mainly released in the form of sulfate, especially for the Na. Compared with inorganic salts, the organic Na was released at lower temperature [27,29]. Almost 100% of the organic Na was released and caused fouling and slagging issues or formed PM during coal combustion. On the contrary, less than 100% of the organic Na was released at low temperature [27,29]. Almost 100% of the organic Na was released and caused fouling and slagging issues or formed PM during coal combustion. On the contrary, less than 100% of the organic Na was released at low temperature [27,29].

3.1.2. Ash removal efficiency and morphology

The compositions of raw coal and leached coal ashes obtained by low temperature ashing were shown in Table 2. CO2-water leached coals had significantly lower contents of AAEM, such as Na2O, MgO, CaO, than those of raw coals and water leached coals. The Na contents of raw WCW, EK and WXGL were 7.61%, 7.04% and 11.47%, respectively, which was considered as organic Na, were in the order of EK > WCW > WXGL, which were 34.2%, 28.2%, 11.6%, respectively. This implies that the Na removal efficiency enhancement by CO2-water leaching may be in the order of EK > WCW > WXGL, compared to that of water leaching. The HCl insoluble Na in the three coals were respectively 5.7%, 18.7%, 6.2%, which was mainly aluminosilicate and cannot vaporize during the coal combustion. This indicates that about 80%-90% of Na in the three coals can release and then caused fouling and slagging issues or PM formation during coal combustion.

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3.2. Ash particle size distribution of DTF combustion

The EK had higher organic Na content and removal efficiency compared to other two coals as shown above. So the EK was used for the combustion experiment by DTF. Particle size distribution of the ashes obtained from raw EK, water leached EK and CO2-water leached EK combustion were shown in Fig. 4. In general, the particle size exhibited a distinct bimodal distribution. The peak point of fine-mode particle was located near 0.1 μm, and a significant inflection point appeared near 0.77 μm. The fine-mode particles were mainly formed by vaporization and condensation of some mineral elements, and the particles size and quantity were proportional to the vaporization quantities and the agglomeration time of the mineral elements. It was found that the Na began to release at the temperature of as low as 600–800 °C during the Zhundong coal combustion [30]. Li et al. [31] found the release of Ca increased with the increase of temperature at 600–900 °C. At 900–1000 °C, Ca release was almost unaffected by temperature, and at above 1000 °C Ca released in large quantities. CO2-water leaching washed out most of the easily vaporized AAEM. Therefore, the submicron particle release of CO2-water leached coal combustion was significantly lower than those of raw coal and water leached coal combustion, as shown in the figure. The formation mechanism of the ultra-micron particles mainly includes [32–34]: breakage of coal coke particles; breakage of internal and external minerals; direct formation of fine internal and external minerals; and melt polymerization between components shown in Table 2. Fe in coal did not be removed by leaching, on the contrary the AAEM, Cl, S etc. were largely removed. This resulted in an increase of the relative content of Fe. Thus the ash color gradually deepened.

![Fig. 4. Ash particle size distributions of raw and leached EK combustions (Raw: raw EK, Water: water leached EK; CO2: CO2-water leached EK).](image-url)

![Fig. 5. PM1, PM2.5, PM10 yields of raw and leached EK combustions.](image-url)
intrinsic minerals. The Zhundong coal char may be strongly broken during the combustion at high temperature, eventually leading to a sharp rise in PM$_{1-10}$ as shown in the figure. Thus, the CO$_2$-water leaching effectively reduced the formation of particle matter, especially the submicron particles, during the Zhundong coal combustion.

The yields of PM$_1$, PM$_{2.5}$, PM$_{10}$ for raw EK and leached EK were shown in Fig. 5. The productions of PM$_1$ of raw coal, water leached coal and CO$_2$-water leached coal were 4.56 mg/(g·ash), 3.91 mg/(g·ash), 3.23 mg/(g·ash), respectively. Compared to raw coal, the amounts of PM$_i$ produced by water leached coal and CO$_2$-water leached coal were reduced by 17.4% and 29.2%, respectively. The PM$_1$ accounted for 12.7% of the PM$_{10}$ for raw coal. On the contrary, these values were reduced to 12.5% and 11.0% for water leached coal and CO$_2$-water leached coal, respectively. The yields of PM$_{2.5}$ and PM$_{10}$ were reduced by 22.68% and 18.48% through CO$_2$-water leaching, compared to those of raw coal. It proves again that CO$_2$-water leaching reduced the formation of particle matter, especially the submicron particles, during coal combustion.

3.3. DTF ash composition

X-ray diffractometer (XRD, Panalytical BV, Empyrean) was used to analyze the crystalline phase composition of the DTF ash from EK coal. The result was shown in Fig. 6. NaAlSi$_3$O$_8$ was detected in the raw and water leached coal ashes, but was not detected in the CO$_2$-water leached coal ash. This is because of that more than 95% of Na was removed by CO$_2$-water leaching for EK coal as shown in Table 3. NaAlSiO$_4$ was detected in all of raw and leached coal ashes. But the diffraction peak of CO$_2$-water leached coal ash appeared weaker than those of raw and water leached coals. The diffraction peaks of CaSO$_4$ and CaAl$_2$Si$_2$O$_7$ in raw and water leached coal ashes were clear. On the contrary, they were not detected in CO$_2$-water leached coal ash, which should be caused by the partial removal of Ca by CO$_2$-water leaching as shown in Table 2.

The mineral composition of EK ash from DTF combustion was es-

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<td>Coal combustion characteristic parameters.</td>
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T$_i$: ignition temperature, T$_{max}$: peak temperature, T$_f$: burnout temperature, V$_{max}$: maximum rate of the weight loss.

The mineral composition of total EK ash from DTF combustion was es-

![Fig. 7. Mineral composition of total EK ash from DTF combustion.](image-url)
estimated by X-ray fluorescence (XRF, Panalytical BV, Zetium). The composition of total EK ash was shown in Fig. 7. The contents of Na, Mg, S and Cl, which were the easily vaporized elements during coal combustion, were reduced by 67.0%, 20.2%, 29.0% and 70.8% by CO2-water leaching, and they were also significantly lower than those of water leached coal. It was especially for the Mg, which was not be reduced significantly by water leaching as shown in Fig. 7. The relative contents of Si, Al and Ca in the DT ash increased. The Si and Al cannot be removed by water leaching and CO2-water leaching, but the Ca was actually removed partly by CO2-water leaching as shown in Table 2. The increase of the relative contents of the Si, Al and Ca in Fig. 7 were caused by the decrease of other elements, such as Na, Mg, S and Cl. Due to the evaporation of Na, the refractory oxides, such as MgO, CaO and iron-containing substances, can be chemically reduced during the burnout of the coke [5,9,35], which played an important role for the formation of PM1, especially fine particles. This is the reason for the lower proportion of PM1 for the CO2-water leached coal ash than those of raw coal and water leached coal ash, as discussed above.

It was found a positive correlation between the PM1 yield and the contents of basic oxides in coal ash, especially for low rank coal [36–40], such as EK. The correlation between the comprehensive indicators of Na2O + MgO, (Na2O + MgO)/(SiO2 + Al2O3) and B/A (B/A = (K2O + CaO + Na2O + MgO + Fe2O3)/(SiO2 + Al2O3 + TiO2)) and PM1 yield of raw and leached EK were investigated and confirmed by using the data shown in Figs. 5 and 7. The comprehensive indicators of the compounds were weight percentage on ash basis [41]. The calculation results, shown in Fig. 8, indicate a good linear correlation between the comprehensive indicators and PM1 yield, especially for the value of Na2O + MgO and (Na2O + MgO)/(SiO2 + Al2O3). It confirmed again the CO2-water leaching reduced the PM1 formation during the coal combustion significantly.

3.4. Mineral distribution in various particle size of DT ash

The ultra-micron particles of 1–10 μm and submicron particles of <1 μm are referred to PM1–10 and PM1, respectively. The mineral compositions of PM1 and PM1–10 were shown in Fig. 9. It shows that the main mineral elements in PM1–10 were Si, Al and Ca. On the contrary, the main mineral elements in PM1 were Na, Mg, S, and Cl, which were the easy removed elements by CO2-water leaching, as discussed above. The proportions of Na, Mg, S and Cl in PM1 from CO2-water leached coal ash were much smaller than those of raw and water leached coal ashes. The Na content in CO2-water leached coal ash was 14.1%, smaller than those of raw and water leached coal ashes, which were 18.8% and 17.2%. It is well known that the formation of the submicron particle during the coal combustion is caused by the condensation and agglomeration of vaporized elements, such as Na, Ca, Mg etc. So, it indicates that the less contents of Na and Mg in CO2-water leached coal was one of the main reasons for the lower PM1 formation as shown in Figs. 4 and 5. CO2-water leaching also decreased the content of Na, Mg, Ca and Cl in PM1–10. The Na and Mg were reduced by 26% and 35% by CO2-water leaching, compared to those of the raw EK ash. Therefore, CO2-water leaching can effectively inhibited the formation of PM.

3.5. Combustion characteristics of CO2-water leached Zhundong coal

According to our previous research and above results, CO2-water leaching can effectively inhibit the slagging and reduce the PM formation and release, but the combustion characteristics of CO2-water leached coal have not been investigated. Therefore, the combustion characteristics of raw coals, water leached coals and CO2-water leached coals were investigated preliminarily by a TGA. The TG and DTG
curves of raw WCW, EK, WXGL and their leached coals were shown in Fig. 10. The TG and DTG curves of water leached coals and CO2-water leached coals shifted to the low temperature zone, compared to those of raw coals. The combustion characteristic parameters, such as ignition temperature (Ti), maximum rates of the weight loss (Vmax), corresponding maximum temperature (Tmax), and final weight loss temperature (Tf) of the samples, are obtained from the DTG curves and shown in Table 3. The Ti, Tmax and Tf of CO2-water leached coals are lower than those of the raw coals. The Tmax is reduced from 389.8 °C of raw coal to 369.6 °C of CO2-water leached coal for WCW. The combustion temperature ranges of the leached coals are all smaller than that of raw coal. So the combustion characteristics of CO2-water leaching coal is improved. The reasons may be that the ash and small organic compounds removed from coal by leaching causes more pore structure and then increase the reactivity of the coal. Besides, some researches also found that some alkalis, such as Na and K, with different existing form have different effect on coal combustion [42]. Inorganic Na inhibits combustion and organic Na has opposite effect [44,45]. The effect of CO2-water leaching on the Zhundong coal combustion is mainly the effect of minerals, such as Na, K, Mg and Ca. Due to the complexity of the influencing factors, further research is required for clearer understanding the effect of CO2-water leaching on the combustion characteristics of the leached coal.

4. Conclusions

In this work, a novel CO2-water leaching method was proposed to suppress the PM formation and release during Zhundong coal combustion. The combustion characteristic of the leached Zhundong coal was also studied and compared. The following conclusions are obtained:

1) CO2-water leaching effectively removes water insoluble minerals from coal, and significantly reduce the formation and release of particulate matter during Zhundong coal combustion, especially for submicron particle formation.
2) The significant reduction of the easily vaporized element contents in CO2-water leached coal, such as Na, Mg, S and Cl, is a main factor for the suppression of particle matter formations.
3) Compare to raw coal, the combustion characteristic of Zhundong coal is improved by CO2-water leaching.

Above all, CO2-water leaching is found to be an effective method to inhibit the formation and release of particulate matter during Zhundong coal combustion. Furthermore, since coal-fired flue gas can be used as a source of CO2, a new way for the efficient utilization of the coal-fired flue gas is provided. Thus, the practical utilization feasibility of the
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CO2-water leaching method for AAEM removal from Zhundong coal is further proved.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.


