Transformation Behavior of Sodium during Pyrolysis of Zhundong Coal: Postprint

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Abstract

Zhundong coal from Xinjiang exhibits high sodium content, which can cause equipment corrosion, ash deposition, and slagging issues during thermal conversion and utilization processes. This study investigates the migration and transformation behavior of sodium during Zhundong coal pyrolysis through stepwise extraction and pyrolysis experiments. Preliminary experimental results demonstrate that sodium in Zhundong coal is predominantly water-soluble sodium, accounting for approximately 60–70%. During the pyrolysis process, the form of sodium undergoes transformation: at temperatures below 700°C, sodium is primarily released as organic sodium; as temperature increases, soluble sodium in both raw coal and water-washed coal transforms into insoluble sodium.

Full Text

An Investigation of Sodium Transformation in Zhundong Coal During Pyrolysis

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Abstract

Zhundong coal from Xinjiang contains high levels of sodium, which causes equipment corrosion, fouling, and slagging during thermal conversion processes. This study investigates the migration and transformation behavior of sodium during Zhundong coal pyrolysis through sequential extraction and pyrolysis experiments. Preliminary results indicate that sodium in Zhundong coal exists primarily in water-soluble form, accounting for approximately 60-70% of the total sodium content. During pyrolysis, the speciation of sodium undergoes significant transformation. Below 700°C, sodium is released mainly as organic sodium compounds, while at higher temperatures, soluble sodium in both raw and water-washed coal converts into insoluble forms.

Keywords: Zhundong coal; pyrolysis; sodium transformation

Introduction

China possesses abundant low-rank coal resources, which constitute approximately 46% of the nation’ s total coal reserves [?]. The Zhundong coalfield in Xinjiang represents China’ s largest intact coal field, characterized by low metamorphic grade, low ash content, and high alkali metal concentrations. However, the high sodium content in Zhundong coal poses serious operational challenges. During combustion, released sodium reacts with gaseous sulfur compounds such as SO_2 in the hot gas to form sulfates that condense on boiler tube surfaces, causing ash deposition and corrosion [?]. Power plants currently blending Zhundong coal have experienced varying degrees of slagging and fouling issues. Since pyrolysis represents the first stage of coal combustion, investigating the migration patterns of different sodium species during this process is essential for developing strategies to control sodium release during pyrolysis and subsequent stages, thereby providing a fundamental basis for the utilization of Zhundong coal.

Extensive research has been conducted on the occurrence modes of sodium in coal and its transformation during coal utilization. Sodium exists primarily in organic and inorganic forms [?], and sequential extraction is widely employed to separate different sodium species. Spiro et al. [?] extracted inorganic sodium present as hydrated ions and chloride crystals using water. Benson et al. [?] used dilute hydrochloric acid to extract most organic and inorganic sodium, leaving behind insoluble sodium primarily in the form of aluminosilicates. Wei et al. [?] demonstrated that sodium carboxylates in coal decompose extensively at pyrolysis temperatures of 500-550°C, releasing sodium in atomic form. Schafer [?] proposed that organic sodium decomposes at low temperatures to produce volatile light carboxyl compounds, with sodium being released mainly as these light carboxylate species. Sathe et al. [?] suggested that sodium is released as sodium carboxylate at low temperatures, while at higher temperatures, it is released primarily as sodium atoms and organic sodium compounds. Quyn et al. [?] found that sodium chloride does not volatilize as intact molecules during pyrolysis, and their results also indicated the importance of understanding migration patterns of different sodium species during the process.

Experimental Methods

1.1 Sample Preparation The study utilized high-sodium Zhundong coal, which was ground and sieved to a particle size range of 150-300 m for experiments. The proximate, ultimate, and ash composition analyses of the coal sample are presented in Table 1 .

1.2.1 Sequential Extraction Procedure Sequential extraction was performed to treat the coal samples. Five grams of coal were washed with Milli-Q deionized water at a solid-to-liquid ratio of 1:50 for 24 hours at 30°C, followed by filtration and drying to produce water-washed coal. The sodium in the filtrate was measured using ICP-OES and defined as water-soluble sodium. The dried water-washed coal was then treated with 0.1 mol/L hydrochloric acid at the same ratio, and the resulting coal was designated as acid-washed coal, with the sodium in the filtrate defined as acid-soluble sodium. Finally, the acid-washed coal underwent microwave digestion, and the sodium content in the digestate was measured and defined as insoluble sodium. Table 2 presents the sequential extraction results for the raw coal.

1.2.2 Pyrolysis Experiments Pyrolysis experiments were conducted in a fixed-bed reactor system, as illustrated in Figure 1 [Figure 1: see original paper]. The pyrolysis employed a quartz reactor with a water-cooled front section maintained at 20°C, with a condensation unit at the outlet using liquid nitrogen to collect products. Nitrogen served as the carrier gas, and the reactor temperature ranged from 500-900°C.

1.2.3 Determination of Sodium Speciation in Char The same sequential extraction method was applied to coal char samples. Half a gram of dried char was placed in a beaker and washed with 200 mL deionized water for 2 hours at 30°C, followed by filtration. The water-soluble sodium content in the filtrate was measured by ICP-OES. After drying the water-washed char, 200 mL of 0.1 mol/L hydrochloric acid was added for washing and filtration to determine acid-soluble sodium content. The char was then microwave-digested to measure total sodium content in the digestate.

Results and Discussion

The sequential extraction of Zhundong coal revealed that water-soluble sodium—primarily inorganic sodium soluble in water—accounts for 66% of the total sodium content. Acid-soluble sodium, mainly organic sodium bound to oxygen-containing functional groups, comprises 28% of the total sodium, while insoluble sodium content is minimal.

2.1.1 Sodium Migration in Raw Coal During Pyrolysis Figure 2 [Figure 2: see original paper] examines sodium volatilization from raw coal under pyrolysis temperatures of 500-900°C, showing that sodium volatility remains relatively constant across this temperature range. This contrasts with Quyn et al. [**?**], who reported increasing sodium volatility with temperature. The discrepancy may be attributed to differences in sodium occurrence forms in the coal or variations in reactor design.

As shown in Figure 3 [Figure 3: see original paper], the proportion of water-soluble sodium decreased from 66% in the raw coal to approximately 30% after pyrolysis, while acid-soluble sodium also showed some reduction. However, insoluble sodium increased from 5% before pyrolysis to 40% afterward, indicating that sodium volatilization occurred concurrently with the conversion of soluble sodium to insoluble forms. The results suggest a transformation tendency between water-soluble and insoluble sodium, though whether this conversion occurs directly or through an organic intermediate process requires further investigation.

2.1.2 Sodium Migration in Water-Washed Coal During Pyrolysis In water-washed coal, 83% of sodium exists as acid-soluble sodium, with the remaining 17% as insoluble sodium. The volatilization behavior of sodium from water-washed coal differs significantly from that of raw coal. As shown in Figure 4 [Figure 4: see original paper], at temperatures below 700°C, sodium volatility from water-washed coal is substantially higher than from raw coal, with 70% of sodium being released. This is primarily attributed to the decomposition of organic sodium, which is released as sodium atoms and light carboxyl compounds [**?**, **?**]. When the temperature exceeds 700°C, sodium volatility decreases dramatically, suggesting a change in sodium occurrence forms.

Figure 5 [Figure 5: see original paper] confirms this hypothesis, showing that after pyrolysis, the remaining sodium in water-washed coal exists primarily as insoluble sodium, with its proportion exceeding 50% in the char. This demonstrates that some acid-soluble sodium converts to insoluble sodium during pyrolysis, and this transformation becomes more pronounced at higher temperatures.

2.1.3 Sodium Migration in Acid-Washed Coal During Pyrolysis In acid-washed coal, sodium exists predominantly as insoluble sodium. Figure 6 [Figure 6: see original paper] shows sodium volatility as a function of pyrolysis temperature, indicating that significant sodium release still occurs during pyrolysis, with volatility generally increasing with temperature. At 800°C, 60% of sodium volatilizes from acid-washed coal. Insoluble sodium in coal consists mainly of aluminosilicate compounds [**?**], and Wei et al. [**?**] suggested that stable sodium species in char after pyrolysis are primarily inorganic sodium aluminosilicates and organically bound sodium that is stably incorporated into the char matrix.

Figure 7 [Figure 7: see original paper] illustrates the changes in sodium speciation in acid-washed coal with pyrolysis temperature, revealing significant shifts in the proportions of acid-soluble and insoluble sodium. The decreasing proportion of acid-soluble sodium and increasing proportions of insoluble and volatile sodium further confirm the interconversion between different sodium forms during pyrolysis.

2.1.4 Sodium Speciation Changes and Release Characteristics During Pyrolysis The experimental results demonstrate that during pyrolysis of raw and water-washed coal, sodium transforms from soluble to insoluble forms, whereas in acid-washed coal, the transformation proceeds from insoluble to soluble forms—the opposite trend. These differing transformation patterns may be attributed to factors including pyrolysis temperature, sodium occurrence forms, and sodium content, though the specific influencing mechanisms require further investigation.

Figure 8 [Figure 8: see original paper] presents the absolute sodium release amounts for raw, water-washed, and acid-washed coals during pyrolysis. The sodium release from raw and water-washed coal remains relatively constant across the temperature range, but decreases sharply at high temperatures for water-washed coal. This can be explained as follows: at low temperatures, sodium volatilization primarily involves light organic sodium species such as sodium carboxylates. Schafer [?] and Quyn [?] proposed that sodium acetate formation plays an important role in sodium release below 600°C through reactions such as:

$\text{CM-CH}_2\text{-COO-Na} \rightarrow \text{CM} + \text{CH}_3\text{-COO-Na}$ (1)
$\text{CM-COO-Na} \rightarrow \text{CM-Na} + \text{CO}_2$

where CM represents a carbon chain.

As temperature increases, pyrolysis-generated volatiles undergo cracking to produce free radicals, while sodium bound to the char matrix is released as sodium atoms that combine with these radicals and volatilize. At even higher temperatures, water-soluble sodium salts such as sodium chloride and sodium sulfate volatilize as intact molecules, while organic sodium becomes stably bound to the char matrix.

The increased insoluble sodium content during pyrolysis may result from several mechanisms. First, organic sodium stabilization occurs as oxygen-containing functional groups decrease with rising temperature, leading to more stable binding between sodium and the char matrix, as shown in reaction 2. Additionally, water-soluble sodium salts such as sodium sulfate may react with silica during pyrolysis to form aluminosilicates [?]:

$\text{Na}_2\text{SO}_4 + 3\text{SiO}_2 \rightarrow \text{Na}_2\text{O} \cdot 3\text{SiO}_2 + \text{SO}_2 + ½\text{O}_2$ (3)
$\text{Na}_2\text{O} \cdot 3\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2$ (4)

These results clearly demonstrate the interconversion between different sodium forms during coal pyrolysis, with temperature and the content of various sodium species exerting significant influence on this transformation.

Conclusion

This study employed sequential extraction and fixed-bed pyrolysis experiments to investigate sodium migration and transformation during Zhundong coal pyrolysis. The results indicate that sodium in Zhundong coal exists primarily as water-soluble sodium (60-70% of total sodium), with lower contents of acid-soluble and insoluble sodium. Below 700°C, sodium volatilization is dominated by the decomposition and release of organic sodium. During pyrolysis of raw Zhundong coal, interconversion occurs between different sodium forms, with soluble sodium reacting with silica and other components at elevated temperatures to form insoluble sodium, thereby increasing the insoluble sodium content. Temperature, sodium occurrence forms, and sodium content all influence this transformation, though further research is needed to fully elucidate these effects.

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