

# Transformation of Alkali Metals during Pyrolysis and Gasification of a Lignite

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Transformation of Na and K in a lignite was investigated during pyrolysis and gasification in a fixed-bed by using a serial dissolution method with H<sub>2</sub>O, CH<sub>3</sub>COONH<sub>4</sub>, and HCl solutions. The evolution of the fractions of four forms in solid and alkali volatilization during pyrolysis and gasification was determined. The results show that a different mode of occurrence between Na and of K in coal existed. Na in coal can be nearly completely dissolved by H<sub>2</sub>O, CH<sub>3</sub>COONH<sub>4</sub>, and HCl solution. However, K in coal exists almost in the stable forms. Both H<sub>2</sub>O soluble and CH<sub>3</sub>COONH<sub>4</sub> soluble Na and K fractions decline during pyrolysis and early gasification stage and increase a little with the process of char gasification. The stable form Na in the char produced during pyrolysis is transferred to other forms during char gasification via the pore opening and a series of chemical reactions. Na<sub>2</sub>SO<sub>4</sub> (K<sub>2</sub>SO<sub>4</sub>) may play an important role in producing stable forms such as Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> during pyrolysis. The fraction of HCl soluble K increases during pyrolysis but decreases markedly during the early gasification stage.

## 1. Introduction

North China has large reserves of low rank coal deposits such as lignite that are suitable to be used in fluidized-bed gasification. Low rank coal contains organically associated inorganic elements in a major part of mineral matter. Although alkali metals such as Na and K are present in various quantities (generally less than 1%) and various forms in raw coals, they have great effects on the utilization of the coals.<sup>1–3</sup> In fluidized-bed combustion, the alkali metal species in the coal are likely to cause the agglomeration of bed materials, leading to defluidization.<sup>4</sup> According to the thermodynamic equilibrium calculation, the vaporization tendency of minor elements K and Na in coal is the greatest.<sup>5</sup> During the pyrolysis/gasification of coal, the release of alkali metal into the vapor phase has been known to cause serious problems such as erosion/corrosion of heat exchanger and gas turbine components in integrated gasification combined cycle (IGCC). As we know, coal conversion is a very complicated process, and the coal type, ash component, oxidation/reduction condition, and temperature strongly affect the

partitioning of these elements.<sup>6,7</sup> Considerable studies have been conducted on the alkali metal behavior during coal combustion in China or in the world. Because of the need for lignite utilization in the world, the volatilization of alkali species during the pyrolysis and gasification of the low rank coals has been extensively investigated in recent years.<sup>8–10</sup> But, the dynamic behaviors of alkali metals during coal pyrolysis and gasification are not clear, especially for the Chinese coals. Therefore, the purpose of this paper is to gain an understanding of alkali metal dynamic behavior of Chinese lignite during pyrolysis and gasification. In the mean time, the transformation of the mode of occurrence of alkali metals in gasified chars is discussed especially.

## 2. Experimental Section

**2.1. Sample Preparation.** A Chinese Inner Mongolia lignite was used in the investigation. The sample was partially dried at low temperature (<35 °C) and then pulverized and sieved to obtain a fraction sample of particle sizes from 0.175 to 0.355 mm. The coal sample is herewith termed as “raw coal”, and its proximate and ultimate analyses are shown in Table 1; the ash compositions are listed in Table 2. Before the experiment, all samples tested were dried in the oven at 110 °C for an hour.

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**Table 1. Proximate, Ultimate Analysis of the Raw Coal**

proximate analysis/wt % (ad)			ultimate analysis/wt % (daf)				
M	A	V	C	H	O	N	S
1.58	29.64	27.29	68.31	4.7	24.39	1.19	1.41

**Table 2. Ash Compositions of the Raw Coal (wt %)**

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>3</sub>
60.77	21.02	2.50	6.00	4.22	1.12	2.38	0.44	1.38	0.17

**2.2. Experimental Apparatus.** The pyrolysis experiments were performed in a fixed-bed reactor, which is shown in Figure 1. The reactor consists of a quartz tube 20 mm in diameter and 600 mm in length. A fused-silica plate is placed in the middle of the reactor to make a bed. At preset temperature, about 2.0 g of dried coal is quickly injected into the quartz tube reactor in N<sub>2</sub>. The sample is kept at the experiment temperature for 30 min and then cooled down to room temperature in nitrogen. And then, the char is weighed and analyzed.

The experiment for coal char gasification was also conducted on a fixed bed as shown in Figure 1. Initially, about 2.0 g of the chars that was prepared at 900 °C by the above-mentioned pyrolysis procedure were placed in the hopper of the reactor. The reactor is heated in nitrogen atmosphere, and when the temperature reaches the required value, 40% N<sub>2</sub> + 60% H<sub>2</sub>O as the gasification agent is introduced into the reactor. Then, the chars are quickly injected into the quartz tube reactor and kept at the experiment temperature for 10 or 30 min and then cooled down to the room temperature in nitrogen. And then, the residues are weighted and analyzed.

The extracted solutions containing Na and K from coal, chars, and gasified char residues are analyzed by AtomsCan 16 (TJA Co., USA) inductively coupled plasma–atomic emission spectroscopy (ICP-AES). The volatility of K and Na during coal pyrolysis and gasification are calculated by the following equation:

$$V\% = \left(1 - \frac{C_{1,d}Y}{C_{0,d}}\right) \times 100 \quad (1)$$

where  $V$  is the fraction of Na and K volatilization, wt %;  $C_{1,d}$  is the content of Na and K in chars and gasified char residues, mg g<sup>-1</sup>;  $C_{0,d}$  is the content of Na and K in coal or chars, mg g<sup>-1</sup>; and  $Y$  is the yield of chars or residues based on the original coal weight.

The fractions of Na and K in raw coal, char, and gasification residue are calculated by the following equations, respectively:

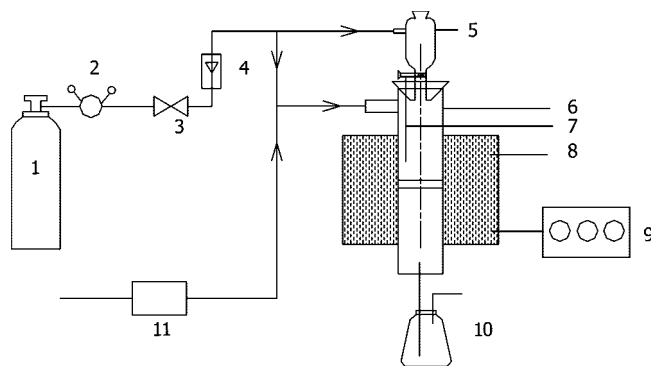
$$\text{fraction(raw)\%} = \frac{i_a}{i} \times 100\% \quad (2)$$

$$\text{fraction(char)\%} = \frac{i_b Y_m}{i} \times 100\% \quad (3)$$

$$\text{fraction(residue)\%} = \frac{i_c Y_m Y_n}{i} \times 100\% \quad (4)$$

where fraction(raw), fraction(char), and fraction(residue) are the fraction of Na and K in raw coal, chars, and gasified char residues, respectively;  $i_a$ ,  $i_b$ , and  $i_c$  are the content of Na and K in different extraction solutions of coal, chars, and gasification char residues, respectively;  $i$  is the content of Na and K in raw coal;  $Y_m$  is the yield of chars during coal pyrolysis; and  $Y_n$  is the yield of gasification char residues during char gasification.

**2.3. Dissolution of Alkali Metals in Coal, Chars, and Gasification Residues.** Sequential chemical extraction<sup>11</sup> is used to determine the modes of occurrence of trace elements in coal. Coal, char, and gasified char residue samples are ground to a particle size of less than 100 μm. During the sequence of extraction steps, alkali metals such as Na and K in coal, chars, or residues were



**Figure 1.** Schematic diagram of the fixed bed reactor: (1) nitrogen cylinder; (2, 3) valves; (4) flow meter; (5) coal hopper; (6) quartz tube; (7) thermocouple; (8) furnace; (9) temperature controller; (10) absorption bottle; (11) steam generator.

classified by the following order: (1) the water soluble forms of alkali metals, i.e. water soluble salts, alkali etc.;<sup>12</sup> (2) the CH<sub>3</sub>COONH<sub>4</sub> soluble forms of alkali metals, i.e. ion-exchangeable organic alkali metal such as carboxylate; (3) the HCl soluble forms of alkali metals, including the alkali metal complex silicates and aluminates; (4) the HCl insoluble forms of alkali metals, called “stable forms”, including the alkali metal present in the organic matrix covered by the carbon or silico-aluminate. The extraction process is described as following: 1 g of raw coal, char, or residue was first immersed into 30 mL distilled water at 60 °C for 2 h and filtered and then immersed into 25 mL 0.1 M CH<sub>3</sub>COONH<sub>4</sub> solution for 2 h at room temperature. Subsequently, the remainders were leached by 25 mL 0.1 M HCl solution at 60 °C for 2 h. The solutions of abstraction were analyzed by ICP-AES. The fractions from different abstractions are named “H<sub>2</sub>O soluble”, “CH<sub>3</sub>-COONH<sub>4</sub> soluble”, “HCl soluble”, and “stable forms”.

### 3. Results and Discussion

**3.1. Variation of Alkali Metal Elements during the Washing Process.** The washing process can lead to the change of composition of alkali metal elements in coal or char. Herewith, in order to obtain the variation of alkali metal in coal during the water-washing and acid-washing processes, the coals were analyzed by energy dispersive X-ray (EDX) as shown in Figure 2. It can be seen that the composition of WW-coal (water-washing coal) varies significantly compared with raw coal, and the relative proportion of Al, O, and Na elements are reduced, which implies that a significant proportion of aluminate or silicate is water soluble in coal and can be removed by water-washing. Compared to the raw coal, the Na is very low and cannot be observed for AW-coal (acid-washing coal).

**3.2. Transformation of H<sub>2</sub>O soluble Na and K.** Figure 3 shows the variations of content of H<sub>2</sub>O soluble Na in raw coal, chars, and gasification residues. In order to compare the variation of Na and K from coal to char and gasification residue clearly, all data are on the basis of the total sodium or potassium contents in the original coal. The pyrolysis experiments were carried out at temperatures of 700, 800, and 900 °C. The pyrolysis chars are named 700char, 800char, and 900char, respectively. The chars (i.e., 900char) were gasified at 900 °C for 10 and 30 min, respectively, and the corresponding carbon conversion is 39.55% for residue 1 and 64.52% for residue 2. From Figure 3, it can be found that there are 27.5% H<sub>2</sub>O soluble Na in raw coal. After pyrolysis, the H<sub>2</sub>O soluble Na decreases obviously from 9.8% in 700char to 5.24% in 900char, which is in agreement with the results obtained by Sugawara et al.<sup>12</sup>

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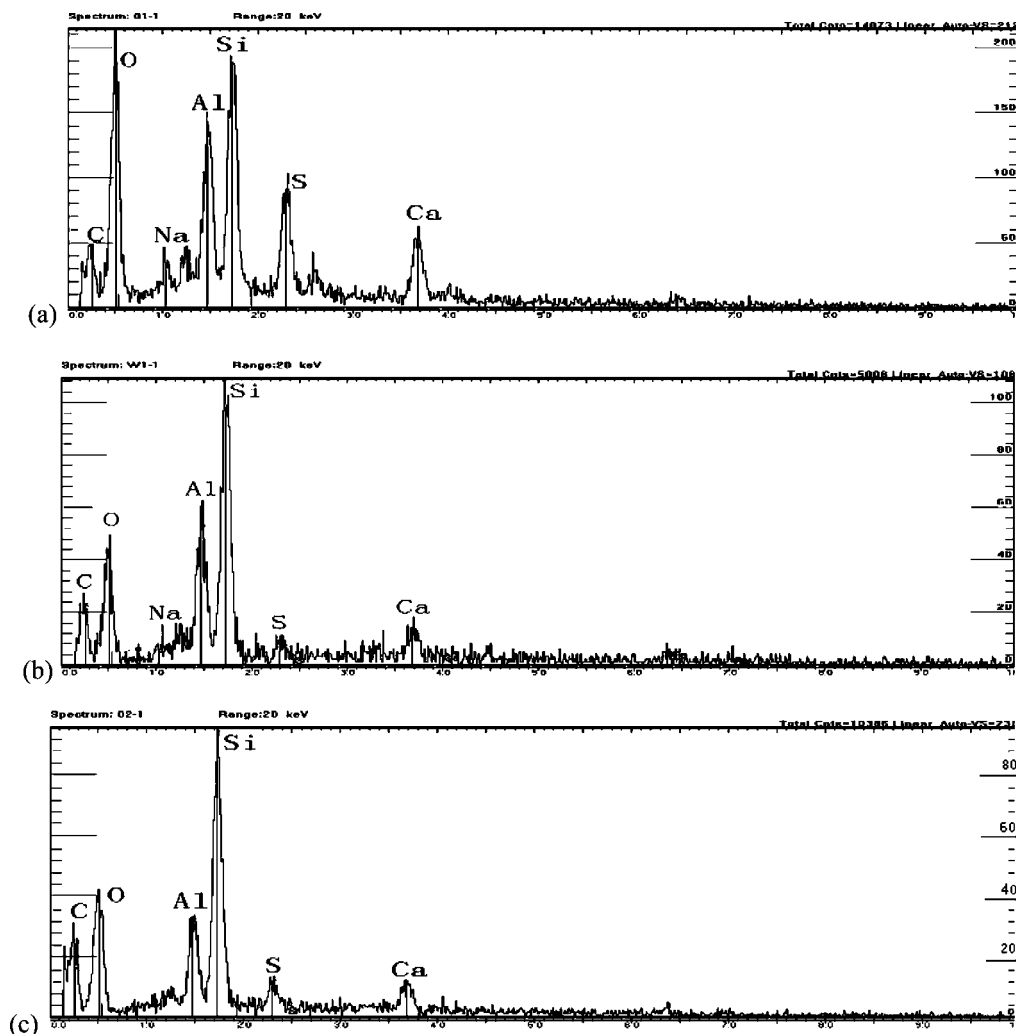


Figure 2. EDX analysis of raw coal (a), WW-coal (b), and AW-coal (c).

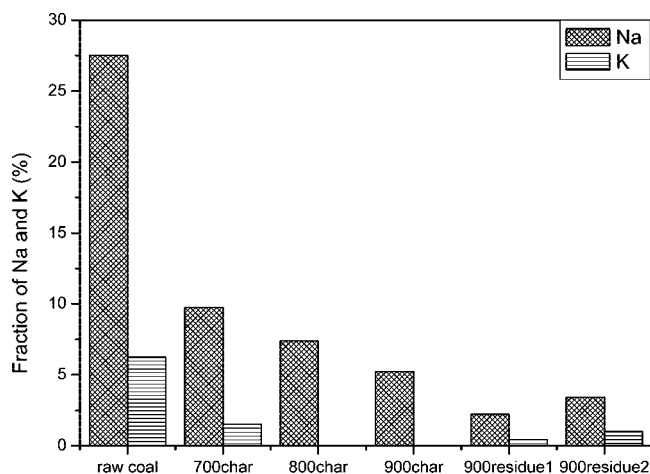


Figure 3. Changes of H<sub>2</sub>O soluble Na and K during pyrolysis and gasification.

The H<sub>2</sub>O soluble Na in gasified residue 1 decreases markedly, but a little increase in gasification residue 2 is observed. The transformation of K has the same trends as that of Na. The H<sub>2</sub>O soluble K in raw coal is about 6.3%. After pyrolysis, the H<sub>2</sub>O soluble K decreases to 1.5% for 700char and disappears for 800 and 900char. Sugawara et al.<sup>12</sup> also found that the H<sub>2</sub>O soluble K disappeared at 1000 °C. Noteworthy is the finding that there is about 0.4% H<sub>2</sub>O soluble K in residue 1 and 1% in residue 2

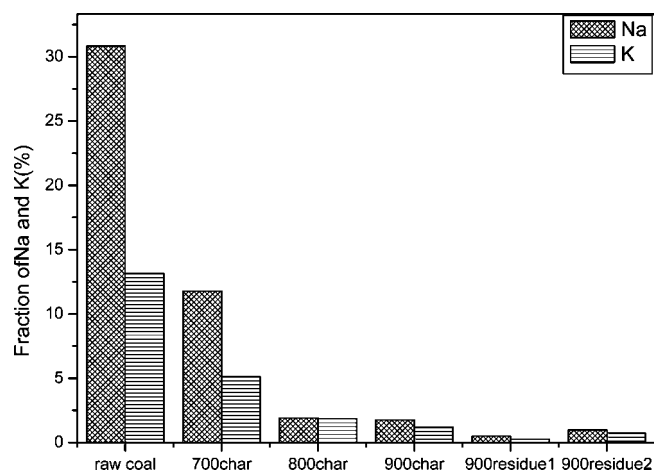


Figure 4. Changes of CH<sub>3</sub>COONH<sub>4</sub> soluble Na and K after pyrolysis and gasification.

after gasification at 900 °C, indicating that H<sub>2</sub>O soluble K can be produced during gasification.

**3.3. Transformation of CH<sub>3</sub>COONH<sub>4</sub> Soluble Na and K.** Figure 4 shows the variations of the content of CH<sub>3</sub>COONH<sub>4</sub> soluble Na and K in raw coal, chars, and gasification residues. It can be noted that CH<sub>3</sub>COONH<sub>4</sub> soluble Na in Inner Mongolia lignite is about 30.8%. After pyrolysis, the content of Na decreases to about 11.8% for 700char and further drops to 1.8% for 900char. The H<sub>2</sub>O soluble K also decreases with the

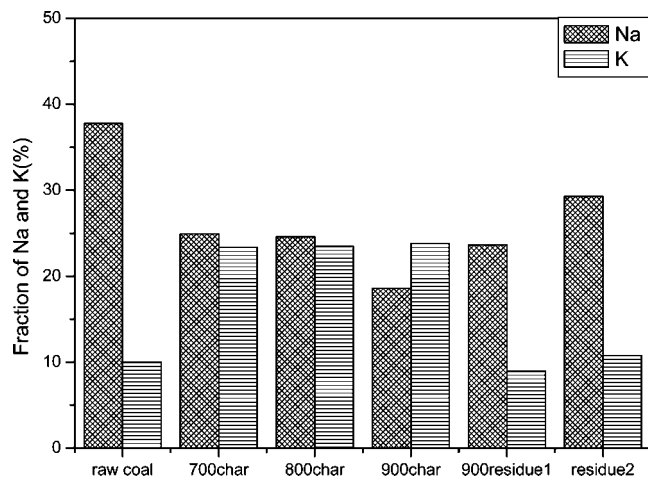


Figure 5. Changes of HCl soluble Na and K during pyrolysis and gasification.

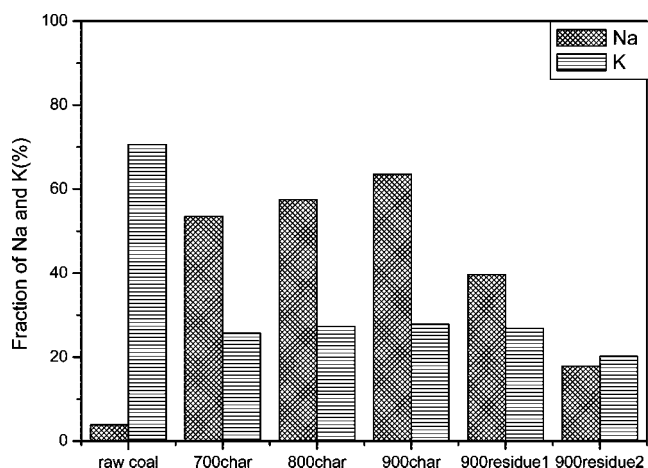


Figure 6. Change of stable form Na and K during pyrolysis and gasification.

increasing pyrolysis temperature. The same results that the  $\text{CH}_3\text{COONH}_4$  soluble Na and K decreases after pyrolysis were also reported by Sugawara et al.<sup>12</sup> After char gasification, it is found that the  $\text{CH}_3\text{COONH}_4$  soluble Na and K also have a little decrease for 900residue 1 compared with 900char but a little increase at higher carbon conversion for 900residue 2.

**3.4. Transformations of HCl Soluble Na and K.** The Na and K which can be removed by HCl solution are mainly associated with complex alkali inorganic matter, e.g.  $\text{Na}_2\text{Si}_2\text{O}_5$  that can be soluble in hot water (90–100 °C).<sup>9</sup> Figure 5 shows the transformation of HCl soluble Na and K during pyrolysis and gasification. After pyrolysis, the HCl soluble Na decreases to 24.9% for 700char and then decreases slowly with increasing pyrolysis temperature. However, K rapidly increases to 23.4% for 700char after pyrolysis and increases slowly with increasing pyrolysis temperature, which is same as the findings of Sugawara et al.<sup>12</sup> During char gasification, the HCl soluble Na increases markedly with carbon conversion. The HCl soluble K decreases obviously during initial gasification (from 23.7% in 900char to 9.0% in residue 1) and then increases a little at higher carbon conversion in residue 2.

**3.5. Transformation of the Stable Form and Volatilization of Na and K.** Figure 6 shows the variation of Na and K in stable forms during pyrolysis and gasification. It can be seen that the fraction of the stable form of Na increases during pyrolysis and decreases during char gasification. However, the fraction of the stable form of K decreases during lower

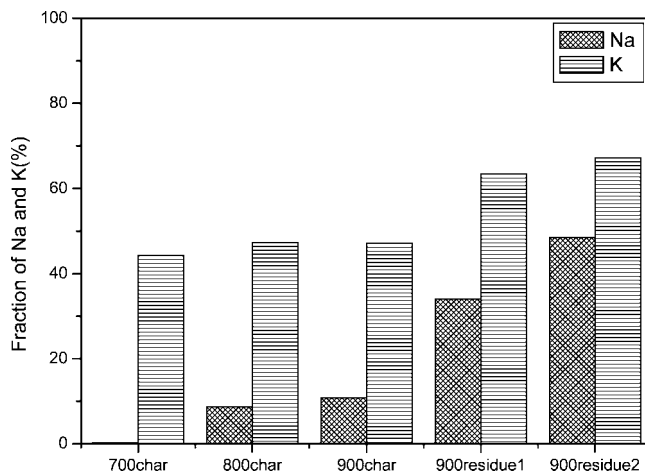


Figure 7. Variation of fraction of Na and K volatilized during pyrolysis and gasification.

temperature pyrolysis and then reduces little with increasing temperature and during gasification.

The evolution of volatilization of Na and K during coal pyrolysis and gasification is shown in Figure 7. It can be seen that there is only about 0.2% Na escaping from coal at 700 °C which increases greatly to 8.6% at 800 °C and then increases little to 10.8% at 900 °C. Sugawara<sup>12</sup> observed that the release of Na varies from 3% at 800 °C to 10% at 1200 °C for Illinois No. 6 coal. However, Quyn et al.<sup>13</sup> found that at 900 °C all Na was volatilized from Loy Yang coal. The difference may result from the different form of Na in the tested coals. During char gasification, the volatile yield of Na increases to 34% for gasification residue 1 and 48.5% for gasification residue 2. It is found that the volatile yield of K is greater at 700 °C and varies little with pyrolysis temperature. This is same as Sugawara's results that the volatility of K changes little during pyrolysis from 800 to 1200 °C for Illinois No. 6 coal. During char gasification, the volatile yield of K rises with carbon conversion. It can be concluded that K in the lignite is vaporized mostly during pyrolysis, while the Na in the lignite is vaporized mainly during char gasification.

**3.6. Discussion.** From the experimental results of coal pyrolysis, it can be found that  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COONH}_4$ , and HCl soluble Na decreases, and stable form of Na increases, greatly during pyrolysis. The volatilization of Na occurs up to the temperature of 800 °C. These results are also indicated by Sugawara et al.<sup>12</sup> and other researchers.<sup>14,15</sup> On the basis of thermodynamics, the volatilizable Na can be turned into the stable form before and after being released from coal.<sup>16</sup> However, there is no specific reaction mechanism to indicate why the stable form of Na increases during coal pyrolysis in the literature. From the EDX analysis in Figure 2, it can be found that the amount of Na, S, and O in raw coal decreases after washing with distilled water. It can be inferred that some

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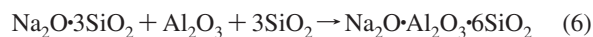
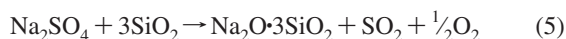
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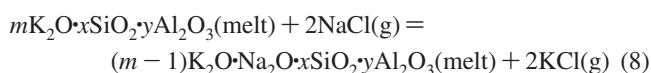
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H<sub>2</sub>O soluble Na can be present in Na<sub>2</sub>SO<sub>4</sub> form in raw coal. During pyrolysis, the reactions can take place between Na<sub>2</sub>SO<sub>4</sub> and silica, aluminum oxides to produce higher melting silico-aluminate.<sup>17</sup>

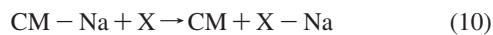
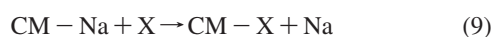


The transformation of HCl soluble and stable form K during pyrolysis is different from that of Na. The different mode of occurrence between K and Na may cause the different characteristics of transformation. In the tested coal, K is mainly in the stable form such as silico-aluminate as indicated in the literature.<sup>16</sup> The decrease of the stable form K during pyrolysis may be caused in two ways: One method is the reaction of potassium silico-aluminate with NaCl to produce volatilizable KCl by eq 8.



Another path is the eduction for K to diffuse to the coal surface from internal silico-aluminate which results in vaporization.<sup>16</sup>

From the experimental results of char gasification, it can be found that during the early gasification stage, the H<sub>2</sub>O soluble Na, CH<sub>3</sub>COONH<sub>4</sub> soluble Na, and the stable form Na decrease, but the HCl soluble Na and the volatility of Na have an obvious increase. Kosminski et al.<sup>9</sup> reported that the sodium vaporization during gasification in CO<sub>2</sub> and steam was significantly higher than that during pyrolysis in N<sub>2</sub> and the sodium carbonate can be formed as the principal form sodium in the char during both pyrolysis and gasification of coal containing carboxylate sodium. The transformation between CH<sub>3</sub>COONH<sub>4</sub> soluble Na and insoluble Na during combustion has been noted by Zhang et al.<sup>19</sup> Therefore, a reaction mechanism for the transformation of Na associated with the organic matrix to HCl soluble Na is proposed. The first organic Na bonded to the char matrix may be released as a metal form or fragment radicals by the following reactions:<sup>20</sup>



where CM represents a site of coal/char matrix and X represents fragment radicals, including tar fragments and hydrogen radicals, formed from the macromolecular network of coal during thermal decomposition inside the particle. Metallic Na could also be formed by decomposition of oxygen functionalities bonded to Na.

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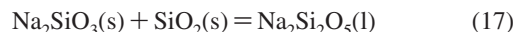
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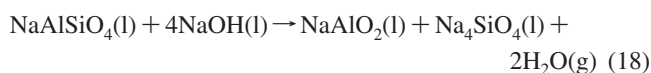
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Then, the metallic Na in char may react with H<sub>2</sub>O, CO, and SiO<sub>2</sub> to transform into water soluble salts such as carbonate or silicates and HCl soluble complex silicates such as Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>:



At higher carbon conversion, a marked decrease of the stable form Na may be due to the transformation to HCl soluble Na and gas phase Na during steam gasification. Another possible mechanism is that a possible stable form present in the organic matrix in the pores blocked out during pyrolysis will be exposed with the pore opening during gasification. And then, alkali metal exposed becomes soluble forms or releases into gas. In the presence of H<sub>2</sub>O, the alkali metal exposed can turn into NaOH. Thus, it is possible that the stable form Na such as NaAlSiO<sub>4</sub> (KAlSiO<sub>4</sub>) reacts with NaOH to form the soluble forms at higher temperature by eq 18 that is usually used in the analysis of ash composition.



Except the HCl soluble K, the transformation behavior of K fractions is same as that of Na. During early gasification stage, the HCl soluble K decrease may be attributed to the eduction for K from inside. With the increase of carbon conversion, the pore in the char is opened, by which more K will be transferred to the outer surface to become soluble or volatilizable forms.

#### 4. Conclusion

The serial dissolution method by solvents was applied to obtain the fundamental data to clarify the dynamic transformation of different forms of alkali metals during pyrolysis and gasification. Some new findings during pyrolysis and gasification are obtained. There is a different transformation behavior between pyrolysis and gasification. The stable form Na in the char is mainly produced during pyrolysis that may be present in the forms of inorganic matter such as silico-aluminate and organic matter such as Na associated with the carbon matrix; the latter is in the pores of char that is blocked out and cannot be accessed. This stable form Na is transferred to other forms during char gasification via the pore opening and a series of chemical reactions. It is proposed that Na<sub>2</sub>SO<sub>4</sub> (K<sub>2</sub>SO<sub>4</sub>) may play an important role to produce the stable forms such as Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> during pyrolysis. Most of the K is present in coal as the stable form. During pyrolysis, the H<sub>2</sub>O soluble, CH<sub>3</sub>COONH<sub>4</sub> soluble, and stable form K decrease, but the HCl soluble K and the volatilization of K increases. During the early gasification stage, a great decrease of HCl soluble K occurs.

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