Mineral migration of alkali metal during the combustion of coal and sewage sludge

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Abstract. The mineral migration of alkali metal during the combustion of coal and sewage sludge was studied by X-ray fluorescence (XRF), X-ray diffraction (XRD) phase analysis and Factsage 7.0 simulation. It showed that the migration process of potassium(K) during the combustion of coal-sludge blends mainly manifested the process from muscovite (KAl₂Si₃O₁₀(OH)₂) to sanidine (KAlSi₃O₈), which included the transforming process of escaped atom K combined with Na₂SO₄ from glaserite or aphthitalite to sanidine (KAlSi₃O₈). The mutual transformation of ardite (Na₂SO₄) and albite (NaAlSi₃O₈) was mainly in the migration process of element Na with low-albite and high-albite appeared occurring in the process. The mutual transformation of anhydrite (CaSO₄) and anorthite (CaAl₂Si₂O₈) was mainly in the migration of element Ca.

1. Introduction

Municipal sludge is considered as a useful biological resource because of its rich organic matters and a large number of trace elements [1,2]. However, environmental pollution can be caused by improper disposal because of its microbes, eggs, bacteria and heavy metals [3]. The pollution and the waste which brings huge environmental and economic benefits can be reduced by the energy regeneration of sludge, effective use of sludge. As a new method of sludge incineration, the power generation boiler of the co-firing of coal and sludge can not only improve the harmless disposal of sludge, but also generate power with the calorific value of sludge [4] to reduce the coal consumption, which effectively alleviates the current problems of large amount of sludge hard to be handled.

Nevertheless, many experts and scholars have found that the alkali metal at high temperature is easy to react with silicon to produce alkaline silicate particles and a large amount of alkaline silicate particles bound in grate furnace wall and heating surface easily formed slag [5]. The alkali metal is easy to react with the bed material and generate the low melting point eutectic compounds causing particles agglomeration[6,7]. Chloride salt, sulfate, hydrogen chloride and other volatile phase materials which cause high temperature corrosion of boiler materials can be easily formed by the alkali metals, Cl, S, and other elements at high temperature. At the same time, low temperature corrosion to the heat exchanger surface can be caused by the condensation of these substances in the low temperature transferring surface [8-10]. In addition, it is a seriously threat to safe operation of the gas turbine. The alkali metal deposition can block the flow channels, suppressing the flow through and reducing the turbine efficiency[11,12]. The gas turbine blade corrosion and reducing the thermal efficiency of gas turbine can be caused by alkali metal components which are not completely cooled with the gasification gas flowing into the gas turbine [13,14]. Therefore, it is worth paying attention to the problems of the migration and transformation of alkali metals in the mixed combustion of sludge...
and coal. The mineral migration process of alkali metals during combustion of coal mixed with municipal sewage sludge by chemical thermodynamic software is simulated in this paper. A certain reference value in the study of micro compound in the combustion process of sludge mixed coal and to a certain guiding role in solving the problems of corrosion and slagging are provided.

2. Materials and methods
Lanba coal from China and sewage sludge obtained from an urban wastewater treatment plant situated in Changsha, China are chosen for the sample. The mixtures of sewage sludge and Lanba coal through dry processing are grinded in a ball milling into particles which are then passed through a 200-mesh miller sieve.

Different mass fractions of sludge on a dry basis (0, 30, 50, 70 and 100%) are mixed with coal (drying basis) to prepare the blended samples. In order to accomplish the homogenization, the mixture is then milled by a mechanical agitator with 400 rpm lasting 20 minutes. Consequently, series of coal-sludge blends (W1, W2, W3, W4 and W5) are made. The contents of sewage sludge are showed by the proportion between wet sewage sludge and coal.

A D/MAX-2200 type rotating anode XRD is used for identifying mineral morphologies for different samples. The rated power of XRD analyzed is 12kW, and its angular accuracy is $\Delta 2\theta \leq \pm 0.02^\circ$. The data of XRD are analyzed by software Jade6. The ashes obtained at 815$^\circ$C grounded at 74$\mu$m are heated at a rate of 15$^\circ$C/min in air atmosphere from a room temperature to an end temperature of 1100$^\circ$C.

3. Results and discussion

3.1. Characteristics of materials and ashes
The proximate analyses of coals and sewage sludge are listed in Table 1. As was showed in Table 1, sewage sludge has some special characteristics compared with Lanba coal. The moisture of sludge is much higher than the coal while the fixed carbon is only 5.13(wt.%). Therefore, The heating values of sludge are lower than the coal because it has a lot of organic matters in the coal. Moreover, the ash yields of samples follow the sequence W1<W2<W3<W4<W5 because it has a lot of inorganic compounds in the sewage sludge.

| Samples | Proximate analysis (wt.%) | Ultimate analysis (wt.%) |
|---------|--------------------------|------------------------|
|         | M$_{ad}$ | A$_{ad}$ | V$_{ad}$ | FC$_{ad}$ | C$_{ad}$ | H$_{ad}$ | O$_{ad}$ | N$_{ad}$ | S$_{ad}$ |
| W1      | 3.09     | 15.77    | 18.57    | 62.57     | 68.10   | 4.28    | 11.03   | 9.50    | 7.09    |
| W2      | 4.65     | 29.6     | 18.73    | 47.02     | 53.61   | 3.89    | 29.19   | 10.18   | 3.13    |
| W3      | 6.24     | 38.79    | 19.22    | 35.75     | 45.16   | 3.12    | 41.85   | 7.41    | 2.46    |
| W4      | 6.74     | 49.37    | 19.86    | 24.04     | 32.81   | 3.72    | 57.85   | 3.9     | 1.72    |
| W5      | 9.34     | 63.77    | 21.76    | 5.13      | 11.94   | 3.13    | 80.58   | 3.97    | 0.38    |

ad, air-dried basis; M, moisture; A, ash; V, volatile; FC, fixed carbon

The compositions of major and minor elements by XRF at 815$^\circ$C are shown in Table 2. As can be seen in Table 2, most of the minerals in the sludge exist in the form of oxide. And the sludge ash has much higher SiO$_2$ contents than coal ash.
Including quartz, muscovite, heulandite, Dawsonite, boehmite, kaolinite, and several minerals including pyrite, rozenite, quartz, szomolnokite, and orthoclase are shown in the sludge. The main minerals in coal, sludge and blends are shown in Table 3 and Table 4.

### Table 2. Ash chemical composition (wt%) of samples

| Samples | SiO₂ | Al₂O₃ | CaO | MgO | Fe₂O₃ | Na₂O | K₂O | SO₃ |
|---------|------|-------|-----|-----|-------|------|-----|-----|
| W1      | 48.40| 23.59 | 1.39| 0.43| 22.85 | 0.20 | 0.92| 2.20|
| W2      | 52.34| 23.65 | 1.41| 0.64| 18.72 | 0.20 | 1.25| 1.62|
| W3      | 54.13| 23.51 | 1.48| 0.72| 16.33 | 0.22 | 1.99| 1.41|
| W4      | 57.60| 23.80 | 1.43| 0.91| 13.26 | 0.21 | 0.20| 0.85|
| W5      | 61.58| 23.91 | 1.51| 1.17| 9.16  | 0.23 | 2.04| 0.30|

### 3.2. Minerals identified in ashes

The major minerals identified by XRD in the ashes obtained at 815°C are shown in Fig.1 and Fig.2. From the X-ray diffractometry, several minerals includingkaolinite, quartz, szomolnokite, rozenite, heulandite and boehmite are shown in the coal ash and several minerals including quartz, muscovite, illite, kaolinite and orthoclase are shown in the sludge. The main minerals in coal, sludge and blends are shown in Table 3 and Table 4.

**Figure 1.** XRD spectrum of W1

1—heulandite \((\text{Ca}(\text{Al}_3\text{Si}_4\text{O}_{10})\cdot6\text{H}_2\text{O})\);
2—kaolinite \((\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4)\);
3—boehmite \((\text{AlO(OH)})\);
4—Dawsonite \((\text{NaAl}(\text{CO}_3)(\text{OH})_2)\);
5—szomolnokite \((\text{Fe}(\text{SO}_4)\cdot\text{H}_2\text{O})\);
6—quartz \((\text{SiO}_2)\);
7—rozenite \((\text{Fe}(\text{SO}_4)\cdot4\text{H}_2\text{O})\);
8—pyrite \((\text{FeS}_2)\)

**Figure 2.** XRD spectrum of W5

I—illite \((\text{K}(\text{Al}_3\text{Si}_2\text{O}_8(\text{OH})_3))\);
K—kaolinite \((\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4)\);
Q—quartz \((\text{SiO}_2)\);
M—muscovite \((\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2))\);
O—orthoclase \((\text{KAlSi}_3\text{O}_8)\)

### Table 3. Mineral content in the W1 and W5

| Sample | Name                | Wt%/ | R   |
|--------|---------------------|------|-----|
| W1     | Kaolinite 1A        | 18.6 | 13.19%|
|        | Szomolnokite        | 8.9  |     |
|        | Rozenite            | 2.9  |     |
|        | Heulandite          | 9.1  |     |
|        | Quartz              | 42.9 |     |
|        | Boehmite            | 7.1  |     |
Equilib of Factsage 7.0 software whose calculation principle is mainly based on the ChemSage Gibbs minimum free energy algorithm is used to calculate. The function is to find the system according to Gibbs energy global minimization of the different phase composition and content [15].

The 100kg various samples of the mineral mole are calculated through W1, W2, W3, W4 and W5 of the main mineral mass fraction data and mineral type amount of data. In order to simulate the real combustion environment, the temperature is set to 200-2100°C and the pressure is set to normal pressure (101325KPa) assuming that the air is composed of 79%N₂+21%O₂. The excess air factor is set to 1.2. The air volume is theoretical calculation from Eq.1-1 as shown blow:

\[
V_e = 0.0889(C_{O_2} + 0.375C) + 0.265H - 0.0333O
\]  
(1-1)

The mineral composition and air quantity of the sample are shown in the chemical thermodynamic balance of Equilib. As was shown in Table 5, the database ideal gas(g), solid state(s), liquid (l), and the use of normal algorithm are selected in the species Compound. As was shown in Fig 3 to Fig 7, the results of the calculation of alkali metal minerals are selected out to draw the alkali metal mineral phase change through the calculation of Equilib module in Factsage.

**Table 4.** Main mineral content of samples (wt.%)

| Sample | quartz | muscovite | illite | kaolinite | orthoclase | szomolnokite | rozenite | heulandite | boehmite | pyrite | dawsonite |
|--------|--------|-----------|-------|-----------|------------|--------------|----------|------------|----------|--------|-----------|
| W1     | 42.9   | -         | -     | 18.6      | -          | 8.9          | 2.9      | 9.1        | 7.1      | 1.3    | 8.1       |
| W2     | 44.1   | 5.19      | 6.3   | 16.29     | 1.14       | 6.23         | 2.03     | 6.37       | 4.97     | 0.9    | 5.67      |
| W3     | 44.9   | 5.19      | 14.75 | 1.90      | 4.45       | 1.45         | 4.55     | 3.55       | 0.6      | 4.05   |
| W4     | 45.7   | 5.19      | 14.7  | 13.21     | 2.66       | 2.67         | 0.87     | 2.73       | 2.13     | 0.3    | 2.43      |
| W5     | 47     | 17.3      | 21.0  | 10.9      | 3.8        | -            | -        | -          | -        | -      | -         |

**Table 5.** Data input in Factsage software

| Sample | SiO₂  | KAl₃Si₃O₁₀(OH)₂ | KAl₃Si₂O₈(OH)₃ | Al₂(Si₂O₅)(OH)₄ | KAl₅Si₃O₈ | FeSO₄(H₂O) |
|--------|-------|----------------|----------------|-----------------|-----------|-----------|
| W1     | 715.00| -              | -              | 70.99           | -         | 52.35     |
| W2     | 735.50| 12.98          | 15.71          | 62.18           | 4.10      | 36.65     |
| W3     | 749.17| 21.63          | 26.18          | 56.30           | 6.83      | 26.18     |
| W4     | 762.83| 30.28          | 36.66          | 50.42           | 9.57      | 15.71     |
| W5     | 783.33| 43.25          | 52.37          | 41.6            | 13.67     | -         |

| Sample | Fe(SO₄)·4H₂O | Ca(Al₃Si₃O₁₀)·6H₂O | Al(OH) | FeS₂ | NaAl(CO₃)(OH)₂ |
|--------|--------------|-------------------|--------|------|----------------|
| W1     | 12.95        | 13.09             | 118.3  | 10.83| 56.25          |
The samples of mineral species and content are analyzed by the XRD experiment and Jade 6.0 software. As was shown in W2, W3 and W4, element K is contained mainly in muscovite, illite, kaolinite and orthoclase while element Ca is mainly in heulandite and element Na is mainly in dawsonite. The products calculated by the Factsage7.0 software at the specific temperature through the principle of the single metallic element in the reactants and the products are also analyzed in this thesis.

3.3. Phase transfer of minerals containing elements K

From Fig 3 and Fig 7, the muscovite in the samples disappears in the temperature of 200-300°C. Therefore, the transformation of muscovite in this range can be found. Element K is contained only in muscovite in the samples of CN. The muscovite converted to sanidine in the temperature range can be found. In Fig 7, the molar amount of muscovite and sanidine are almost equal and the molar amount of andalusite, sillimanite and corundum are also almost equal so that muscovite in W1is only converted to sanidine.

There are various mineral species in W2, W3 and W4. Muscovite disappears and sanidine appears at 200-300°C in each sample. It proves that the muscovite transforms into sanidinein in this temperature range. At the same time, escaped atom K and Na2SO4 (ortho) are combined into
K$_3$Na(SO$_4$)$_2$(s) so that the molar amount of sanidine is significantly smaller than that of muscovite. K$_3$Na(SO$_4$)$_2$(s) is a kind of complex salt, which is formed by two kinds of simple salt crystals whose chemical composition are still the simplest elements [16]. K$_3$Na(SO$_4$)$_2$(s) is identified as the glaserite or the aphthitalite all belonging to the same kind of salt with the same chemical formula [17]. In this process, muscovite itself not only transforms to sanidine, but also interacts with other substances in the reaction system that appears glaserite (or aphthitalite), which fully proves the existence of synergistic effect between various mineral potential.

With the increasing of temperature, the content of sanidine gradually increases. When the reaction system temperature reaches 700°C, the molar amount of sanidine tends to be stable with the potassium sulfate (or potassium sulfate stone) disappearing. According to the migration of element K, atom K transforms to sanidine with the crystal structure of K$_3$Na(SO$_4$)$_2$(s) changing. In term of the molar quantity, the quantity of the feldspar increases significantly in the temperature of 600-700°C.

3.4. **Phase transfer of minerals containing elements Na**

Na is contained mainly in Dawsonite which is a kind of orthorhombic carbonate minerals containing water, sodium and aluminium. With the increasing temperature of the reaction system, the product category of W5 combustion process is analyzed. The Dawsonite transforms to albite in the reaction system. The carbonate mineral decomposition, the combination process of Na and silicate Albite exists in this process because albite belongs to the aluminosilicate. However, the reaction mechanism remains to be further studied.

In the temperature range of 400-700°C, there is a small amount of Na$_2$SO$_4$ (hexago) in the reaction system. Na$_2$SO$_4$ (hexago) is one of the six hexagonal crystal. According to the molecular formula and crystal type, it can be presumed to be thenardite [18]. With the temperature rising, thenardite in the reaction system disappears and the molar quantity of albite increases dramatically, which shows that Na of thenardite is regressed to albite.

The mineral species of W2, W3 and W4 are complex. Atom Na all concentrates in the orthorhombic thenardite at 200°C. With the temperature rising, atomic vibration amplitude becomes larger in Fig4. Orthorhombic thenardite transformed into low-albite [19] at 200-300°C. With the temperature further increasing, the low-albite transforms into hexagonal thenardite at 400-500°C, which shows that the thenardite of hexagonal crystal structure is more stable than orthorhombic crystal structure. Then hexagonal thenardite transforms into High-Albit at the temperature of 600-700°C. At the temperature of 700-2000°C, the molar amount of sodium high-albite remains constant. In Fig 5 and Fig 6, the migration of element Na is in conformity with the process of that in Fig 4.

3.5. **Phase transfer of minerals containing elements Ca**

The heulandite is formed in a low temperature environment [20], it has converted to anhydrite when the reaction system temperature rises to 200°C. Therefore, element Ca is mainly contained in the anhydrite in Fig 4-7 at the temperature of 200°C. As the temperature of the reaction system rising, the anhydrite is converted to the anorthite at the temperature of 900-1000°C. Anhydrite is one of sulfate minerals while calcium feldspar is one of aluminosilicate minerals. Therefore, there must be products of anhydrite decomposition which reacts with aluminosilicate with anorthite formed. It also shows that there is a mutual synergy between the mineral material to achieve a state of equilibrium and stability. In the temperature of 1000-2000°C, there is no transformation of anorthite. In this process, the molar amounts of anhydrite and anorthite are equal substantially. The element Ca of the migration is completely consistent with it in Fig 4-7, which shows that the preceding analysis of the element Ca derived from the migration process is reliable.

4. **Conclusions**

The through the simulating study on the migration of alkali metal minerals in combustion process of sludge and coal, we can get following conclusions:
(1) Quartz, muscovite, illite/illite, kaolinite and orthoclase are contained in the municipal sewage sludge. Kaolinite, szomolnokite, rozenite, heulandite, quartz, boehmite, pyrite, dawsonite are contained in the Lanba coal. The content of quartz is very high in the coal and sludge.

(2) The migration of K in process of sludge mixed coal combustion is a transformation of muscovite, glaserite (or aphthitalite) and sanidine. At the temperature of 200-300°C, muscovite transforms into sanidine. At the same time, atom K escaped from muscovite is combined with Na$_2$SO$_4$ (ortho) with glaserite (or aphthitalite) formed. At the temperature of 600-700°C, glaserite (or aphthitalite) disappears and atom K returns to sanidine. At the temperature of 700-2000°C, mineral containing potassium is sanidine.

(3) The migration of element Na during the combustion of municipal sewage sludge mixed with coal has four main processes. At the temperature of 200-400°C, orthorhombic thenardite transforms to low-albite. At the temperature of 400-500°C, low-albite transforms to hexagonal thenardite. At the temperature of 600-700°C, hexagonal thenardite transforms to high albite minerals. At the temperature of 700-2000°C, mineral containing element Na is albite.

(4) The migration of Ca in process of city sludge mixed with coal combustion is a transformation of anhydrite and anorthite. At the temperature of 200-900°C, element Ca mainly exists in the anhydrite. At the temperature of 900-1000°C, anhydrite transformed into anorthite. At the temperature of 1000-2000°C, mineral containing element Ca is anorthite.

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