The high-temperature volatilization of sylvite and solid reaction process between sylvite and minerals

Liu Ji
North China Electric Power Research Institute Co., Ltd.
421796198@qq.com

Abstract. The effects of volatilization of sylvite were investigated when the mineral was added in it and the reaction mechanism of solid phase between potassium and minerals such as CaCO₃, SiO₂, Al₂O₃, Fe₂O₃ were conducted at the same time by means of high temperature calcination, thermal analysis and XRD analysis. Results show that four kinds of mineral components can restrain the volatilization of potassium in different extents, KCl and K₂SO₄ are relatively stable at high temperatures, which can only react with Al₂O₃ to produce KAl₅O₈; K₂CO₃ is the most active, and it can not only react with CaCO₃ to produce K₂Ca(CO₃)₂ in low temperature but also decompose to K₂O that co-melt with SiO₂, which can also react with Al₂O₃ or Fe₂O₃ to form stable and high melting point KAlO₂ and KFeO₂ respectively.

1. Preface
Clogging is a common problem in the production of new dry cement. Especially with the increasing tension of resources, low grade raw fuel is more and more used in cement production, which leads to more prominent plugging. There are many reasons for the clogging of the crust. Cai Shibin[1] and other people think that the main factors of formation of the crust are alkali metal, chlorine, sulfur content and volatilization rate in raw material, sulfur and alkali ratio in clinker, coal quality and mineral composition, etc. Long Shizong and others[2] through the study of cement predecomposition system dust and alkali, chlorine and sulfur thawing properties of the study found that chloride, sulphate base and their complex are the formation of low temperature thawing, which is the cause of clogging of the crust. It is also found that the crusts are multi component eutectic[3] formed by alkali metal sulfur and chlorine at high temperature. After the dehydration of the clay minerals in the material, the activity is high, and the volatile components in the flue gas are easily adsorbed to form KCl-K₂SO₄-Na₂SO₄ three yuan low melting substance and adhere to the wall of the tube to form the powder lump[4-5].

The crust involves the solid state reaction, sintering, melting and the high temperature volatilization of the kiln head and the condensation at the tail of the kiln at different temperatures and atmospheres. The process is very complicated. The composition of the mineral phase of the crust is not clearly defined. Most of the existing studies are concentrated on the cause of the clogging and the different temperatures in the kiln. The study of the reaction between raw mineral and alkali metal minerals is not yet thorough. Therefore, the key to understand the crust mechanism is to reveal the heterogeneous reaction between alkali metal minerals and raw mineral.

In view of the above problems, and because of the complex components in the process of cement sintering, the purpose of this study is to discuss the volatilization characteristics of alkali metals and their mineral components (cement raw materials and clinker) by means of thermal comprehensive analysis, high temperature calcination test and X ray diffraction analysis. The mechanism of crust
blockage is explored by the way of solid phase reaction.

2. Experimental part

2.1. Sample preparation
The molar ratio composition of the samples in the experiment is given. All the mineral components are chemical pure reagents and the granularity is less than 74um. The specific sample preparation process is as follows: first, the pure minerals are dried, and then the precision balance is used according to the molar ratio, and then sealed and stored in the dry Petri dish after the mixed grinding.

Table 1. Composition of sample

| Sample number | Composition     | Molar ratio | Sample number | Composition     | Molar ratio |
|---------------|----------------|-------------|---------------|----------------|-------------|
| 1             | KCl            |             | 9             | K₂SO₄+Al₂O₃    | 1:1         |
| 2             | KCl+CaCO₃      | 1:1         | 10            | K₂SO₄+Fe₂O₃    | 1:1         |
| 3             | KCl+SiO₂       | 1:1         | 11            | K₂CO₃         |             |
| 4             | KCl+Al₂O₃      | 2:1         | 12            | K₂CO₃+CaCO₃   | 1:2         |
| 5             | KCl+Fe₂O₃      | 2:1         | 13            | K₂CO₃+SiO₂    | 1:2         |
| 6             | K₂SO₄         |             | 14            | K₂CO₃+Al₂O₃   | 1:1         |
| 7             | K₂SO₄+CaCO₃   | 1:2         | 15            | K₂CO₃+Fe₂O₃   | 1:1         |
| 8             | K₂SO₄+SiO₂    | 1:2         |               |                |             |

2.2. Thermal analysis experiment
The STA449C type thermal analyzer was used to test and analyze the volatilization behavior of alkali metals in the samples of Table 1 in air atmosphere. The parameters of the instrument were set as follows: the gas carrying capacity was 100ml/min, the heating rate was 10℃/min, and the final temperature was 1400℃.

2.3. Solid state reaction test at high temperature
The high temperature resistance furnace was used to calcinate the samples of different components in Table 1. The calcined products were analyzed by D8 Advance X ray diffractometer. The calcination test conditions are: from room temperature to 800℃, 1000℃, 1200℃ and 1400℃, 30min is then cooled to room temperature. Test conditions: scanning speed 5 degree (2 theta /min), scanning range (2 theta) 5 degree ~90 degree.

3. Results and discussion

3.1. The effect of minerals on the volatilization of potassium salt
Because of the different mixture ratio and the decomposition of CaCO₃ at the low temperature section, in order to facilitate the analysis of the thermal weight loss process of potassium salt in high temperature mixtures, the TG data obtained in this section are processed, only the data after 800℃ are retained, and the normalization method[6] is used, and the TG data is converted to the quality at the time of 800℃. The rate of change in volume can directly compare the decomposition of potassium salts in various samples. Figure 1 shows the results of thermogravimetric analysis of some samples.
\[ \eta_{tg} = \frac{\eta_{tg,TG}}{\eta_{tg,800}} \times 100\% \]  

Formula: the relative mass change rate; The relative mass fraction on the thermogravimetric curve; The relative mass fraction at 800 °C.

Figure 1 describes the volatilization of three kinds of potassium salts of KCl, K₂SO₄ and K₂CO₃ at different temperatures before and after adding CaCO₃, SiO₂, Al₂O₃ and Fe₂O₃. Within the range of temperature studied, KCl volatilizes sharply between 800 °C to 950 °C, basically evaporated at 950 °C, and KCl is most volatile in three kinds of potash salts, which is due to chlorine. The presence of ions will promote the volatilization of [7]. The addition of CaCO₃, SiO₂, Al₂O₃ and Fe₂O₃ increases the temperature range of the sharp change of KCl and increases the end temperature of the volatilization. It is known that the addition of minerals postpones the volatilization of KCl and reduces the volatilization rate of KCl, among which SiO₂ and Al₂O₃ delay the effect more obviously; K₂SO₄ begins to volatilize. The temperature is high, and it is still not completely volatilized at 1400 °C. After adding CaCO₃ and Al₂O₃, the curve becomes slow and the slope is obviously smaller. Before 1300 °C, the volatilization curve of adding SiO₂ and Fe₂O₃ coincides with the curve without mineral addition, indicating that the volatilization of K₂SO₄ can not be suppressed effectively, and the volatilization ability of K₂CO₃ is between KCl and K₂SO₄. In addition, the addition of four minerals could inhibit the volatilization of K₂CO₃, especially the inhibition of SiO₂ and Fe₂O₃.

The above analysis results show that the four minerals can obstruct the volatilization of three kinds of potassium salts, and study the interaction mechanism from the solid state reaction process of potassium and minerals.

![Graphs showing evaporation characteristics of three potash salts before and after mineral addition](image)

**Fig.1** evaporation characteristics of three potash salts before and after mineral addition

### 3.2. Solid state reaction of potash salt with mineral

#### 3.2.1. Solid state reaction of KCl with mineral

Fig. 2 shows XRD diagram of calcined products of CaCO₃, SiO₂, Al₂O₃ and Fe₂O₃ for KCl. There is no solid phase reaction between KCl and CaCO₃, SiO₂ and Fe₂O₃ in the range of experimental temperature, but as the temperature increases, KCl can bond with CaCO₃ to form a brittle crust. The mixture of KCl and SiO₂ showed liquid phase at high temperature, and KCl was bonded by melt. The change of phase inhibited the volatilization of KCl.

KCl and Al₂O₃ are fused at 1000 °C. At 1200 °C, KCl has been volatilized greatly, and a few have reacted with Al₂O₃ to form KAl₅O₈ (type 2). The temperature increases to 1400 °C, and the remaining Al₂O₃ is in sharp contrast with the peak value of KAl₅O₈ diffraction. The product is mainly Al₂O₃. The above analysis also confirmed that the effect of SiO₂ and Al₂O₃ on KCl volatilization was stronger in the last section.

\[ KCl + 5 / 2 Al_2O_3 + 1 / 4O_2 \rightarrow KAl_5O_8 + 1 / 2Cl_2 \]
3.2.2. Solid state reaction of K$_2$SO$_4$ with mineral

Figure 3 is the XRD diagram of the calcined products of K$_2$SO$_4$ and Al$_2$O$_3$. The interaction between K$_2$SO$_4$ and cement raw material is similar to that of KCl. In the whole temperature range, no new material is produced by CaCO$_3$, SiO$_2$, Fe$_2$O$_3$ and K$_2$SO$_4$, and the diffraction peak of K$_2$SO$_4$ is more obvious. The bonding ability of K$_2$SO$_4$ is not strong, and it is difficult to bond with CaO and CaCO$_3$ at 850°C to 1150°C. From the observation of the test process, it is found that with the increase of temperature, the test products of K$_2$SO$_4$ and three minerals transition from powder to harder caking, which is due to the gradual melting of K$_2$SO$_4$ with the increase of temperature and the rapid cooling. After adding Al$_2$O$_3$, no new product was produced in the temperature range from 800°C to 1200°C. The XRD diagram was dominated by the diffraction peak of K$_2$SO$_4$, and at 1400°C, Al$_2$O$_3$ reacted with partial K$_2$SO$_4$ to form KAl$_5$O$_8$ (formula (3)), but the diffraction peak of K$_2$SO$_4$ was still more obvious. The change of the state of the test product is similar to that when CaCO$_3$, SiO$_2$ and Fe$_2$O$_3$ were added. It can be seen that the volatilization of K$_2$SO$_4$ is inhibited by two factors: physical binding and chemical reaction.

$$\frac{1}{2}2K_2SO_4 + \frac{5}{2}Al_2O_3 \rightarrow KAl_5O_8 + 1/2SO_2 + 1/4O_2$$  (3)

Fig. 3 XRD pattern of calcined products after Al$_2$O$_3$ addition in K$_2$SO$_4$
3.2.3. Solid state reaction of K$_2$CO$_3$ with mineral

Fig. 4 is XRD diagram of calcined products added to CaCO$_3$, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ respectively in K$_2$CO$_3$. The bonding ability of K$_2$CO$_3$ to all kinds of materials is relatively small, and is not bonded at any temperature of less than 950°C. K$_2$CO$_3$·1.5H$_2$O appeared when the K$_2$CO$_3$ was absorbed by the tide. The complex K$_2$Ca(CO$_3$)$_2$ (type (4)) is formed at 800°C, and the substance is not stable. CaCO$_3$ decomposes to CaO with the increase of temperature. At high temperature, no solid reaction was observed between K$_2$CO$_3$ and CaO, and a small amount of K$_2$CO$_3$ still existed at 1200°C and 1400°C.

$$K_2CO_3 + CaCO_3 \rightarrow K_2Ca(CO_3)_2$$  \hspace{1cm} (4)

After adding SiO$_2$, the peak of K$_2$CO$_3$ diffraction line is not obvious after 1000°C of temperature. Studies have shown that Si and potassium salts combine to form molten silicate K$_2$O∙(SiO$_2$)$_n$[8-9]. Nielsen et al also found that the reaction of K$_2$CO$_3$ and SiO$_2$ occurred in[10] type (5). The material that was removed during the test was not obvious melting at 800°C, and the material that was removed at the last three temperatures was very obvious. Starting from 800°C, some K$_2$CO$_3$ reacted with Al$_2$O$_3$ to form KAIO$_2$ (type(6)), and KAIO$_2$ had better stability. The temperature continues to rise to 1000°C. Most of the K$_2$CO$_3$ is involved in the reaction, and KAIO$_2$ can easily absorb water from the air, and then convert to hydrate. At 1200°C and 1400°C, all K$_2$CO$_3$ react with Al$_2$O$_3$ to form KAIO$_2$. Fe$_2$O$_3$ is similar to the Al$_2$O$_3$ rule. At 800°C, part K$_2$CO$_3$ and Fe$_2$O$_3$ participate in the reaction to generate KFeO$_2$ (type (7)). The temperature continues to rise, and the content of KFeO$_2$ is more stable.

$$K_2CO_3 + xSiO_2 \rightarrow K_2O \cdot xSiO_2 + CO_2 \hspace{1cm} (x = 1, 2, 4)$$  \hspace{1cm} (5)

$$1/2K_2CO_3 + 1/2Al_2O_3 \rightarrow KAlO_2 + 1/2CO_2$$  \hspace{1cm} (6)

$$K_2CO_3 + Fe_2O_3 \rightarrow 2K_2FeO_2 + 2CO_2$$  \hspace{1cm} (7)

![Fig. 4 XRD pattern of calcined products after mineral addition in K$_2$CO$_3$](image-url)
4. Conclusions

4.1. The volatilization ability of KCl is the strongest. The four mineral components have a certain inhibitory effect on the volatilization of KCl, but the mechanism is different. KCl, SiO₂ and Fe₂O₃ inhibited the volatilization of KCl by physical bonding. KCl and Al₂O₃ formed a small amount of KAl₅O₈ by chemical reaction to inhibit the volatilization of KCl.

4.2. The volatilization temperature of K₂SO₄ itself is very high. After the melting of K₂SO₄ with CaCO₃, SiO₂, and Fe₂O₃, the volatilization is inhibited. There are two reasons for the inhibition of K₂SO₄ volatilization after the addition of Al₂O₃. Physical inhibition and chemical reaction are not easy to volatilize KAl₅O₈.

4.3. K₂CO₃ has the strongest reaction ability. After adding CaCO₃, the complex K₂Ca(CO₃)₂ was formed at 800°C, but the substance was unstable and decomposed to CaO with the increase of the temperature, so the effect of CaCO₃ on the volatilization of K₂CO₃ was very weak. The co-melting of K₂CO₃ and SiO₂ is very obvious, so the effect of SiO₂ on the volatilization of K₂CO₃ is very obvious; The mechanism of Al₂O₃ and Fe₂O₃ on K₂CO₃ is similar. At 800°C, some K₂CO₃ and Al₂O₃ and Fe₂O₃ have formed a stable KAlO₂, KFeO₂. At 1400°C, all K₂CO₃ and Al₂O₃ were involved in the reaction, and the KFeO₂ content was stable with the increase of temperature. and all participate in the reaction; With the temperature The content of KFeO₂ was more stable.

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