Using Sewage Sludge as Alternative Fuel and Raw Material to Produce Cement Clinker

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Abstract. In the present study, we proposed a method that using sewage sludge (SS) as alternative fuel and raw material to produce cement clinker. It was found that the increasing amount of SS can favor for the formation of tricalcium silicate (C₃S) but the excessive amount can cause the impediment effect. Furthermore, SS contains high contents of trace elements, especially for zinc and manganese. The thermodynamic equilibrium calculation of Zn and Mn are also conducted to further understand their transformation behaviors and the results show that zinc is predicted as a volatile element while manganese shows great condensed potential during the cement clinker calcination process.

Keywords: Sewage Sludge, Cement Clinker, Trace Element, Thermodynamic Equilibrium

1. Introduction

With the rapid development of urbanization and industrialization, a large quantity of wastes are produced. Amongst these wastes, sewage sludge (SS) is a kind of waste that derive from sewage treatment plant [1, 2]. According to the statistic, more than 8 million tons of dried SS is produced in China every year with the increasing rate of 10% annually [3]. How to deal with such a large number of SS has become a severe environmental issue that needs to be timely resolved. In China, the common ways for the SS treatment are agriculture, landfill and incineration, but the shortage of available of land and the increasing concern about of environment from public limit these methods application [4-6]. Utilization of SS in the cement kiln seems to be a promising method, which can completely destroy the hazardous substances due to the high temperature and long residual time that cement kiln involves [7]. Besides, due to SS contains significant heat value and the main component of its ash are SiO₂, Al₂O₃, CaO and Fe₂O₃, which are the main component of cement raw meals [8]. Therefore, SS can be used as alternative fuel and raw materials to produce cement clinker.

The utilization of SS in the cement kiln presents multiple advantages but also can exist some problems, such as trace element problem. Trace element has attracted more and more attention due to their hazardous effect on human health and ecosystem [9]. A better understanding of the trace elements transformation behaviors during cement clinker calcinations process can efficiently prevent its secondary pollution. However, this is still unclear. Besides, the transformation behaviors of trace elements can be influenced by various conditions, such as their thermodynamic properties, the combustion temperature and the characteristics of raw materials. Thermodynamic equilibrium calculation is widely used to study the trace elements behaviors under different conditions. To the best knowledge of present author, no thermodynamic
equilibrium study has been conducted on the trace elements behaviors during cement clinker calcination process.

The object of this study is to understand the effect on the cement clinker with different amounts of SS addition. Additionally, the trace elements transformation behaviors during cement clinker calcinations process are also studied using FactSage 6.4.

2. Materials and Method

The dried sewage sludge (SS) pellet was collected from a municipal wastewater treatment plant located in Beijing, China. The chemical composition of SS was determined by X-ray fluorescence spectrometer (XRF, S4-Explorer, Bruker), as shown in Table 1. It can be seen that major component of SS are SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, which are the essential component for the cement clinker manufacture and the mineralogical composition of SS was determined by X-ray diffraction (XRD, D/Max 2500, Rigaku).

The raw materials were prepared by the reagent of CaCO$_3$, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and various amount of SS. The raw materials were pressed to φ20×5mm slices with the pressure of 10Mpa and then put into the electrically heated tube furnace. The temperature was set from room temperature to 1450 °C at the rate of 10 °C/min.

The trace elements in the SS were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Prodigy XP, Leeman) and the thermodynamic equilibrium calculation is conducted using FactSage 6.4.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>25.19</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.63</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.15</td>
</tr>
<tr>
<td>CaO</td>
<td>6.35</td>
</tr>
<tr>
<td>MgO</td>
<td>1.54</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.18</td>
</tr>
<tr>
<td>P$_2$O</td>
<td>4.85</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Mineralogical characterization of the eco-cement clinker

The XRD pattern of eco-cement clinker with different amounts of SS addition are shown in the Fig. 1. It can be seen that the mainly crystalline composition in the blank sample are C$_3$S (Ca$_3$SiO$_5$), C$_2$S (Ca$_2$SiO$_4$), C$_3$A [Ca$_3$Al$_2$O$_6$ and Ca$_3$(Al,Fe)$_2$O$_6$] and C$_4$AF (Ca$_4$Fe$_2$Al$_2$O$_{10}$), which is similar with that in the commercial use cement clinker. The most important characteristic peak of C$_3$S appeared at 2θ about 32°, which is the major component of Portland cement clinker that determines its quality, as shown in Fig. 2. The intensity of it can indicate the relative content of C$_3$S in the clinker to some extent [10, 11]. It can be seen that the characteristic peak of C$_3$S shows no obvious change as SS addition up to 10wt. %. However, it obviously increase with 15wt. % SS addition. With the addition of SS further increase, the phase of C$_3$S disappears and the phase of f-CaO, C$_5$S-0.05C$_3$P are formed, which might be attributed to the high content of phosphorus in SS, as shown in Table 1. During the cement clinker calcinations, the excessive phosphorus can decompose the C$_3$S into C$_5$S and f-CaO, and then causing the formation of phosphorus in C$_3$S solid solution (C$_3$S-0.05C$_3$P). This indicates that the high intake of SS can cause the undesirable effect on the C$_3$S formation. Therefore, the addition of SS should be strictly controlled.
3.2. Micrographs observation

The C₃S in the cement clinker is commonly produced by the reaction between C₂S and CaO in liquid phase. The liquid phase in the clinker can be observed by SEM, which is shown in Fig. 3. It can be seen that the big crystal grains are close to each other and are stacked together with distinct contours and boundary in the blank sample. With the SS addition, the outline of the crystal grains became more blurred. As the addition of SS reaches 15 wt. %, the boundary lines of the crystalline grains get mixed with the interphase and cannot be clearly identified. Furthermore, the crystal grains exhibit independent existence and are connected directly to the liquid phase as the amount of SS addition increases to 15 and 30 wt. %. Therefore, the addition of SS can raise the amount of liquid phase. As for the crystal size, the present results show that SS addition has no obvious influence on the growth of the crystalline grains until the amount of SS reached 15 wt. %. In addition, a large amount of pores were observed to be distributed in the blank sample. The pores were found to decrease with the SS addition and the crystalline grains were connected to each other. These
results differ from those reported by Lin et al [12], which might be due to the increasing liquid phase with SS addition, resulting in a more compact cement clinker with decreased porosity.

![SEM micrographs of the eco-cement clinkers with different amounts SS](image)

**Fig. 3:** SEM micrographs of the eco-cement clinkers with different amounts SS

### 3.3. The transformation of trace element during cement clinker calcinations

It is known that equilibrium calculations have limitations due to its neglect on kinetic effects, nonuniform distribution as well as the mode of occurrence of the elements [13]. However, from the current study, it can be seen that equilibrium calculation helps to understand the general disciplines of the elements behavior under different variables. To further understand the influence of different process variables and chemical compositions on trace elements behavior, thermodynamic equilibrium calculations were conducted using FactSage 6.4 assuming a closed environment and 1 kg of raw materials is used as input data. Several calculation condition is considered: The system only containing C, H, N, S is calculation as basic system. The introduction of Cl in the system is considered to identify the possible impact. The mineral contents are added into the system to examine the possible interaction. The calculations is performed at the range of temperature 1000 - 2000K and this range of temperature includes the clinker calcinations at 1723K.

The trace element content in the SS are shown in the Table 2. It can be seen that the trace element in SS is notably high, especially zinc and manganese. Thus, the elements of zinc and manganese are selected for the thermodynamic equilibrium study and the results are shown in Fig. 4 and Fig. 5. It can be seen that, the equilibrium composition for zine mainly depends on the temperature. ZnO(s) in only stable species in the equilibrium at the temperature between 1000~1400K. With temperature further increase, the proportion of ZnO(s) sharply decrease with the increase of Zn(g). All of the zinc exists as vapor phase when the temperature above 1800K. The presence of choline can lead to the formation of ZnCl₂(g) but in a small proportion. Furthermore, it can be seen that zinc shows no interaction behavior with mineral phase. The average temperature in cement kiln is about 1723K. Therefore, zine is predicted as a volatile element in cement kiln according to the simulated result. As for manganese, it can be seen that manganese shows great condensed potential during cement clinker manufacturing process. When the temperature is under 1500K, almost of manganese is in the form of Mn₂O₃(s2). With the temperature further increase, MnO(s) becomes the most stable species. The introduction of choline and mineral phase have no obvious influence on the species of manganese.

![Table 2: The trace elements content in SS (mg/kg)](image)

<table>
<thead>
<tr>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>80</td>
<td>256</td>
<td>2</td>
<td>11</td>
<td>124</td>
<td>358</td>
<td>543</td>
<td>41</td>
<td>48</td>
</tr>
</tbody>
</table>

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Fig. 4: The influence of different parameters on speciation of Zinc: a) Basic system: C, H, N, S, O; b) +Cl, a=1.2; c) Basic system + Cl + mineral contents.

Fig. 5: The influence of different parameters on speciation of Manganese: a) Basic system: C, H, N, S, O; b) +Cl, a=1.2; c) Basic system + Cl + mineral contents.
4. Conclusion

From our present study, we can draw the conclusion that the appropriate amount of SS additions can favor for the C₃S formation, while the excessive amount can cause the impediment effect. Besides, the addition of SS can effectively increase the liquid phase content during the cement clinker calcination process. SS contains high contents of trace elements, especially for zinc and manganese. According to the thermodynamic equilibrium calculation, zinc tends to exist as vapor phase, while manganese shows the great condensed potential during the cement clinker calcinations process.

5. Acknowledgements

Zuotai Zhang and Zhenzhou Yang designed the experiments; Zhenzhou Yang conducted the experiments, analyzed the data, and wrote the manuscript; Yingyi Zhang, Lili Liu, Xidong Wang advised the experiments and helped editing the manuscript.

6. References


