Calculation of Forming Heat of Cement Clinker Made from Calcium Carbide Slag

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Abstract. Calcium carbide slag can be a substitute for the natural limestone to produce cement clinker and also with a high portion of CaO as an excellent calcium raw material. Thus, it not only reduces the pollution that the calcium carbide slag brings to the environment, but also reduces the exploitation of non-renewable resource-limestone. The main mineral constituent of calcium carbide slag is Ca(OH)\textsubscript{2}, and there are many differences in decomposition temperatures between the calcium containing raw materials. When calcium carbide Slag is added, the forming process of cement clinker and the major reactions happened in that process changes. The empirical equation for calculating forming heat of cement clinker made of limestone is no longer applied for those made of calcium carbide slag. In this paper, the empirical equation for forming heat calculation of calcium carbide slag added cement clinker is researched and rebuilt under the principles of thermodynamics. Results show that the change of raw materials has a great influence on the forming heat of cement clinker. When the traditional raw materials are replaced by calcium carbide slag, the forming heat of cement clinker will be reduced. Calculating the forming heat by the revised empirical equation can help reduce errors and make calculation results near the reality and then convenient for evaluation of heat efficiency. The work provides some theoretical underpinnings for the process analysis and calculation of forming heat of cement clinker made from calcium carbide slag.

Introduction

If part of active calcium waste, such as carbide slag and high calcium fly ash, is used to replace natural raw materials, it can reduce the consumption of coal and natural limestone, on the other hand, it can also reduce the CO\textsubscript{2} emission of calcium carbonate decomposition, and then the burning heat consumption of clinker and its environmental load value can be reduced. The main component of carbide slag as a waste of chemical plant is Ca(OH)\textsubscript{2}. During the formation process of cement clinker, the decomposition heat of calcium hydroxide is different from that of calcium carbonate which is the main component of limestone, therefore the formation process and formation heat of clinker is different. In the thermal power research of cement kiln, an empirical formula in thermal measurement of cement kiln has been used to calculate clinker formation heat all the time\cite{1} (Building Materials Science Research Institute, 2010). However, the empirical formula is based on taking limestone as calcium raw ingredients, while for carbide slag and other industrial waste ingredients, a method as described in Appendix B\cite{2} (Chinese Building Industry Press, 2007) of JC/730-2007 should be adopted for calculation. This method is quite tedious with the vast amount of work, and some of the data is not easy to achieve\cite{3}. Since the chemical composition and mineral composition of carbide slag is quite different from limestone raw materials\cite{4}, the empirical formula for formation heat calculation of limestone and clay ingredients is not suitable for that of carbide slag. In this paper, the
formation process of clinker composed of carbide slag will be investigated by analyzing the composition and structure of carbide slag. Meantime, the theory of chemical thermodynamics is adopted to deduce a simple formula for formation heat calculation of the clinker composed of carbide slag, and the acid dissolution experiment is used to determinate and verify formation heat of carbide slag ingredients.

**Composition and Structure of Carbide Slag**

**Chemical Composition of Carbide Slag**

Raw materials used for tests in this paper, such as limestone and bauxite were taken from JYSP cement plant, sandstone was taken from JYZJ cement plant, nickel slag was taken from JYQY cement factory, four kinds of carbide slags were taken from SPHH chemical plant. The chemical analysis results of raw materials were shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Loss</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>R$_2$O</th>
<th>SO$_3$</th>
<th>∑</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>41.67</td>
<td>5.03</td>
<td>1.1</td>
<td>0.21</td>
<td>50.55</td>
<td>1.13</td>
<td>0.2</td>
<td>0.08</td>
<td>99.97</td>
</tr>
<tr>
<td>Sandstone</td>
<td>1.6</td>
<td>85.77</td>
<td>5.47</td>
<td>1.94</td>
<td>3.0</td>
<td>0.65</td>
<td>0.18</td>
<td>1.7</td>
<td>99.12</td>
</tr>
<tr>
<td>Bauxite</td>
<td>13.65</td>
<td>45.07</td>
<td>25.21</td>
<td>4.8</td>
<td>5.33</td>
<td>0.91</td>
<td>2.74</td>
<td>1.7</td>
<td>99.41</td>
</tr>
<tr>
<td>Nickel slag</td>
<td>0</td>
<td>32.45</td>
<td>4.98</td>
<td>42.3</td>
<td>7.38</td>
<td>1.91</td>
<td>0.78</td>
<td>5.31</td>
<td>95.11</td>
</tr>
<tr>
<td>Carbide slag</td>
<td>29.74</td>
<td>4.89</td>
<td>1.76</td>
<td>0.61</td>
<td>61.39</td>
<td>0.1</td>
<td>0.21</td>
<td>0.21</td>
<td>98.70</td>
</tr>
</tbody>
</table>

As seen in Table 1, the main chemical composition of carbide slag and limestone were basically the same, which mainly oxides were CaO, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$. Meantime, a few harmful components, such as K$_2$O, Na$_2$O, SO$_3$ and Cl$^-$, were also contained in carbide slag. According to the chemical composition, the content of CaO in carbide slag with a range of 60%-67% was much higher than that in limestone; therefore, it can be used as top quality calcareous materials. Loss on ignition of carbide slag was quite low, which was about 0.6-0.75 of loss on ignition of limestone, so the theoretic consumption of raw material with carbide slag was less. The contents of trace components in carbide slag, such as K$_2$O, Na$_2$O, MgO etc. alkali contents, were low; especially, the content of MgO was close to zero. This is because that during the production process of carbide slag, and in high temperature of 2000 degrees and reductive atmosphere conditions, MgO in carbide slag was reduced to simple substance and escaped with K$_2$O, Na$_2$O after gasification. However, as the low alkali content of carbide slag and its raw material was not favorable to reduce the minimum eutectic temperature, the quantity of liquid phase may be less, and the liquid viscosity was increased leading to poor burn-ability, which was not helpful for sintering of clinker and formation of C$_3$S.

**Mineral Composition**

![Figure 1. The X-ray diffraction of carbide slag.](image1)

![Figure 2. The differential thermal analysis of carbide slag.](image2)
Carbide slag was analyzed by X-ray diffraction and differential thermal analysis with the test results shown in Figure 1 and Figure 2. The XRD results show that when $2\theta$ are 18.020°, 28.719°, 34.120°, 47.220°, 50.821°, 54.381°, 62.599°, 64.579°, 71.923°, the diffraction peaks of Ca(OH)$_2$ are clearly observed and the corresponding d values are 4.9185, 3.1059, 2.6256, 1.9232, 1.7951, 1.6857, 1.4827, 1.4419, 1.3117, respectively. The main mineral phase of carbide slag is Ca(OH)$_2$. Meantime, when $2\theta$ are 22.924°, 29.420°, 35.939°, 39.343°, 43.100°, 47.220°, 48.502°, the diffraction peaks of CaCO$_3$ are clearly observed and the corresponding d values are 3.8763 Å, 3.0335 Å, 2.4968 Å, 2.2882 Å, 2.0971 Å, 1.9232 Å, 1.8754 Å. Hence, the main mineral phase of carbide slag is CaCO$_3$ besides Ca(OH)$_2$. This may be because the carbide slag is long-term stored, the mineral phase composition Ca(OH)$_2$ reacts with CO$_2$ in the air as well as SiO$_2$.

The differential thermal and thermogravimetric results show that in the heating process of carbide slag, it is mainly Ca(OH)$_2$ decomposition with decomposition temperature of 400-600℃. Compared with the thermal decomposition characteristics of calcareous material of limestone, decomposition temperature of Ca(OH)$_2$ in carbide slag is much lower than that of CaCO$_3$ in limestone. Moreover, according to relevant thermodynamic data, endothermal decomposition of Ca(OH)$_2$ is 1160 kJ kg$^{-1}$, while the endothermal decomposition of CaCO$_3$ is 1660 kJ kg$^{-1}$. Therefore, from the decomposition temperature and endothermal decomposition of main mineral phase, when carbide slag is used to replace limestone, it is helpful to reduce heat consumption in the decomposition stage of raw material theoretically.

In the clinker formation process, if the calcareous material provides the same calcium oxide for solid phase reaction, decomposition heat required by calcium carbonate is much greater than that of calcium hydroxide. From this perspective, when carbide slag is used to replace limestone and produce the cement, the decreased decomposition temperature of calcareous materials will be favorable for the reduction of formation heat of the clinker theoretically, so the total heat consumption can be reduced. After the limestone is replaced by carbide slag, the forming reaction process of clinker has been changed, so the traditional experience formula can't be directly used in formation heat calculation of clinker which is added by carbide slag ingredients.

An Empirical Formula Derivation of Formation Heat for Calcining Cement Clinker with Carbide Slag

Clinker formation heat refers to the heat required by dry material when it at reference temperature(0 or 20°C) is made of 1Kg clinker at the same temperature under certain production and no material or heat loss conditions. It only relates to the variety and property of original fuel and chemical composition of clinker, while has no relations with intermediate reaction process of clinker formation. According to the method described by Stetson, raw components in all clinkers are converted into free oxides by counting thermal effects of minerals in clinkers, and these oxides are given their required heat, and then formation heat of cement clinkers are calculated simply. Based on this theory, through accounting the initial state and final state of the material, the enthalpy required by the change between two states is formation heat, so an empirical formula of formation heat of steel slag cement clinker, and the basic thermodynamic data required to calculate can be found out in handbook of thermodynamic data of inorganic chemistry[5].

H Zur Strassen[6](H Zur Strassen, 1957) finally has deduced a complex and lengthy calculation method through counting thermal effects of minerals in clinkers, converting raw components in clinkers into free oxides, giving these oxides the required heat, simplified calculating the formation heat of cement clinker, and finally getting the calculation formula of formation heat directly with chemical analysis data of raw materials and clinkers:

$$Q_{sh} = 4.11 \cdot a_T + 6.48 \cdot m_C + 7.646 \cdot c_C - 5.116 \cdot s - 0.59 \cdot f.$$  \hspace{1cm} (1)
Where, \( a_T \) is the percentage content of \( \text{Al}_2\text{O}_3 \) in 100g clinker (%), \( m_c \) is the percentage content of \( \text{MgO} \) in 100g clinker (%), \( s \) is the percentage content of \( \text{SiO}_2 \) in 100g clinker(%), \( f \) is the percentage content of \( \text{Fe}_2\text{O}_3 \) in 100g clinker(%), \( c_c \) is the percentage content of \( \text{CaO} \) coming from \( \text{CaCO}_3 \) decomposition in 100g clinker (%).

It means that \( a_T \) is completely from clay mineral, and this calculation method usually exists errors of 2 kcal/Kg. As seen from the experience formula, this formula is derived on the basis of limestone and clay system and is clearly not suitable for an industrial slag system. Well then, how much impacts will this simple calculation formula of formation heat on the new dry cement clinker?

The results of chemical analysis, mineral composition analysis, thermal decomposition characteristics analysis of carbide slag and experimental tests show that there are a lot of difference in formation heat of clinkers with carbide slay and limestone, respectively. The traditional empirical formula cannot be used to calculate the formation heat of clinkers with carbide slag ingredients. This paper has derived a simple calculation formula of formation heat of cement clinker using carbide slag ingredients as calcium raw material with chemical thermodynamics theory, which provides a convenient way to calculate formation heat of cement clinker with carbide slag ingredients.

The basic thermodynamic data required for calculation can check the inorganic chemistry handbook of thermodynamic data. The absorbed heat of 1g (100%) \( \text{CaO} \) generated is:

\[
Q_{\text{Ca(OH)}_2} = 4.689 \text{ kcal/kg.}
\]  

So the absorbed heat of 1% \( \text{CaO} \) production is: 

\[
Q_1 = 4.689 \text{ kcal/kg.}
\]  

If the content of calcium oxide decomposed by calcium hydroxide is \( c_H \), then

\[
Q_{\text{Ca(OH)}_2} = 4.689 \cdot c_H \text{ kcal/kg.}
\]  

Carbide slag is used to replace limestone to make clinker, and its calcium oxide is from the decomposition of the calcium hydroxide and calcium carbonate as well as other raw materials besides calcium hydroxide and calcium carbonate, which we list as follows:

\[
c = c_H + c_c + c_R.
\]  

Where, \( c \) is the content of \( \text{CaO} \) in clinker (wt%), \( c_H \) is the content of \( \text{CaO} \) from the decomposition of \( \text{Ca(OH)}_2 \) (wt%), \( c_c \) is the content of \( \text{CaO} \) from the decomposition of \( \text{CaCO}_3 \) (wt%), \( c_R \) is the content of \( \text{CaO} \) from the decomposition of other raw materials besides \( \text{Ca(OH)}_2 \) and \( \text{CaCO}_3 \) (wt%).

According to literature, thermal effect formulas of calcium carbonate decomposition and mineral formation of cement clinker are:

\[
Q_{\text{CaCO}_3} = 7.532 \cdot c_c.
\]  

\[
Q_{C,S,A,F} = 0.114 \cdot c - 5.116 \cdot s - 0.286 \cdot a - 0.589 \cdot f.
\]  

Where, \( c \) is the percentage content of \( \text{CaO} \) in 100g clinker (wt%), \( s \) is the percentage content of \( \text{SiO}_2 \) in 100g clinker (wt%), \( a \) is the percentage content of \( \text{Al}_2\text{O}_3 \) in 100g clinker (wt%), \( f \) is the percentage content of \( \text{Fe}_2\text{O}_3 \) in 100g clinker (wt%).

Therefore, all thermal effects of \( \text{CaO} \) are combined together, and formula (8) (9) (10) are added up to get the thermal effects of \( \text{CaO} \):
\[ Q_{\text{CaO}} = Q_{\text{Ca(OH)\textsubscript{2}}} + Q_{\text{CaCO\textsubscript{3}}} + Q_{\text{Ca,S,Ca,C\textsubscript{A},Ca,AF}}(\text{CaO}) = 4.689 \cdot c_{\text{H}} + 7.532 \cdot c_{\text{C}} + 0.114 \cdot c_{\text{R}}. \]  

Then formula (8) is taken into formula (11) to get:

\[ Q_{\text{CaO}} = 4.803 \cdot c_{\text{H}} + 7.646 \cdot c_{\text{C}} + 0.114 \cdot c_{\text{R}}. \]  

Generally speaking, \( c_{\text{R}} \) in the formula has a little effect on the value of clinker formation enthalpy and can be neglected; error is less than 100 cards, thus we get the final formula for the thermal effect of calcium oxide:

\[ Q_{\text{CaO}} = 4.803 \cdot c_{\text{H}} + 7.646 \cdot c_{\text{C}}. \]  

As the derivation process of the thermal effect of other oxides is basically unchanged, the thermal effect of several other oxides remains unchanged, and a simple calculation formula of formation heat is obtained for cement clinker which is made from carbide slag:

\[ Q_{\text{sh}} = 4.11 \cdot \text{a}_{\text{T}} + 6.48 \cdot \text{m}_{\text{c}} + 4.803 \cdot c_{\text{H}} + 7.646 \cdot c_{\text{C}} - 5.116 \cdot s - 0.59 \cdot f. \]  

\[ (10) \]

Where, \( \text{a}_{\text{T}} \) is the percentage content of \( \text{Al}_2\text{O}_3 \) in 100g clinker (wt%), \( \text{m}_{\text{c}} \) is the percentage content of \( \text{MgO} \) in 100g clinker (wt%), \( s \) is the percentage content of \( \text{SiO}_2 \) in 100g clinker (wt%), \( f \) is the percentage content of \( \text{Fe}_2\text{O}_3 \) in 100g clinker (wt%), \( c_{\text{H}} \) is the content of \( \text{CaO} \) from the decomposition of \( \text{Ca(OH)}_2 \)(wt%), \( c_{\text{C}} \) is the content of \( \text{CaO} \) from the decomposition of \( \text{CaCO}_3 \)(wt%).

### Formation Heat Determination of the Clinker Composed of Carbide Slag

This paper has designed the saturation ratio of cement clinker SM=2.6, silicic acid rate KH=0.90, alumina ratio IM=1.6, and the carbide slag, sandstone, nickel slag and aluminum vanadium soil ingredients are chosen as raw material to mix with proportioning ratio shown in Table 2. The test results are compared with calculation results of chemical thermodynamics, traditional empirical formula (1), derived formula (10) and shown in Table 3.

### Table 2. Ratio of different raw materials (%).

<table>
<thead>
<tr>
<th>Carbide slag</th>
<th>Sandstone</th>
<th>Bauxite</th>
<th>Nickel slag</th>
<th>Fly ash</th>
<th>Steel slag</th>
<th>Coal ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.44</td>
<td>10.51</td>
<td>6.01</td>
<td>2.04</td>
<td>--</td>
<td>--</td>
<td>2.204</td>
</tr>
</tbody>
</table>

### Table 3. Comparison of clinker formation heat of different methods.

<table>
<thead>
<tr>
<th>method</th>
<th>calculated value by traditional formula method</th>
<th>calculated value by chemical thermodynamics</th>
<th>derived formula in this paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>clinker formation enthalpy(cal/kg)</td>
<td>420.3</td>
<td>282.5</td>
<td>254.6</td>
</tr>
</tbody>
</table>

The calculated results show that if the empirical formula is used to calculate the formation heat of clinker, it will produce an error of 137.8kcal/kg, and therefore the experience formula derived in this paper should be used to calculate clinker formation heat of carbide slag ingredients to ensure the accuracy of the heat efficiency. The formation heat of cement clinker composed of carbide slag is about 254.6kcal/kg. Theoretically, the cement clinker produced by carbide slag ingredients can
greatly reduce formation heat of cement clinker. The main reason is that decomposition temperature and heat of Ca(OH)$_2$ which is the main component of carbide slag ingredients is lower than that of CaCO$_3$ which is the main component of limestone, thereby the formation heat of the clinker of carbide slag ingredients is low. Compared with traditional empirical formula, the calculating formula derived in this paper has small test error, convenient and fast calculation for the clinker formation heat of carbide slag ingredients.

**Conclusions**

Through the work, results got as:

1. When the carbide slag replacing limestone and Ca(OH)$_2$ as the main component, the decomposition temperature and decomposition heat of carbide slag is lower than the main component CaCO$_3$ of limestone. The decomposition temperature of Ca(OH)$_2$ is about 500$^\circ$C, and is lower than 900$^\circ$C of CaCO$_3$. Decomposition heat of Ca(OH)$_2$ is 1963.3202kJ/kg•CaO, while the decomposition heat of CaCO$_3$ is as high as 3178 kJ/kg•CaO.

2. After the carbide slag is replaced of limestone, the formation process of the clinkers is almost the same, but the mineral phase formation temperature of the clinker is slightly lower than that of the traditional clinker.

3. Using the same rate data for preparation of raw meal, the formation heat of cement clinker with carbide slag ingredients is about 254.6kcal/kg, while that for limestone ingredients is 420.3kcal/kg. Hence, the cement clinker produced by carbide slag ingredients can greatly reduce the clinker formation heat.

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**References**


