Calcination of Calcium Sulphoaluminate Cement Using Pyrite-Rich Cyanide Tailings

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Abstract: Pyrite-rich cyanide tailings (CTs) are industrial hazardous solid wastes arising from the gold mining industry. Every year, hundreds of millions of tons of cyanide tailings are produced and discharged to tailings dams. It is of great significance to dispose of cyanide tailings harmlessly and resourcefully. The feasibility of calcination of calcium sulphoaluminate (CSA) cement clinker using pyrite-rich cyanide tailings as Fe2O3 and SO3 sources was investigated for this paper. The behavior of pyrite during the calcination of cyanide tailings under various calcination conditions and the properties of calcium sulphoaluminate cement clinker were examined. The results show that it is feasible to produce calcium sulphoaluminate cement clinker using pyrite-rich cyanide tailings. The optimal conditions for the calcination of calcium sulphoaluminate cement using pyrite-rich cyanide tailings were confirmed. During the calcination process, the cyanides decompose into carbonate, CO2, and N2. The pyrite decomposes into Fe2O3 and SO2, and they react with CaO and Al2O3 to form the intermediates of CaSO4, 2CaO-Fe2O3, and CaO-2Al2O3, which further react to form 3CaO-3Al2O3-CaSO4, 4CaO-Al2O3-Fe2O3, and 12CaO-7Al2O3. The calcium sulphoaluminate cement prepared by pyrite-rich cyanide tailings exhibits excellent mechanical properties and meets the compressive strength criteria of 42.5 grade calcium sulphoaluminate cement.

Keywords: calcium sulphoaluminate cement; pyrite; cyanide tailings; cement clinker

1. Introduction

Calcium sulphoaluminate (CSA) cement was essentially developed in China in the 1970s [1,2]. It is usually produced by limestone, clay, and bauxite in addition to natural gypsum at 1250–1350 °C, about 100–200 °C lower than that for ordinary Portland cement (OPC) production [3,4]. CO2 emissions could be reduced significantly in this process because the major phase in CSA clinker is 3CaO-3Al2O3-CaSO4 (C4A3S5) compared to 3CaO-SiO2 in OPC [5]. Thus, CSA cement is considered as a sustainable and eco-friendly alternative to OPC due to the lower energy consumption and fewer CO2 emissions during the production [6].

This cement is widely used in architecture engineering, emergency maintenance, permeability resistance engineering, cement manufacturing, and other fields owing to its low alkalinity, rapid hardening, high early-age strength, high impermeability, chemical resistance/freeze–thaw corrosion, and low shrinkage [5,7]. However, the aluminum and sulfur sources suitable for the production of CSA cement are limited [8]. In recent years, increasing attention has been paid to the recycling of industrial by-products such as fly ash [9,10], gypsum [4,11], slag [12], and other solid wastes [13,14] for CSA production.
Cyanide tailings (CTs), produced from the gold cyanidation process in the gold mining industry, are one of the hazardous solid wastes [15]. It is estimated that more than 2.45 million tons of CTs are discharged to tailings dams in China every year [16]. It is required by law that CTs must be detoxified to a total cyanide concentration of less than 5 mg·L\(^{-1}\) before being discharged to tailings dams; otherwise, a penalty rate of $150 per ton is imposed in addition to the disposal fees charged by the certified solid waste disposal company [17]. Many technologies for the treatment and utilization of CTs have thus been developed [15,18]. Some treatment methods were implemented for CTs detoxification, such as alkali-chlorination [19], dry stack technology [20], incineration [21], the biological method [22], and natural degradation [23]. However, these methods may have problems of uncertain effects, the formation of toxic intermediates, limited capacity, and large occupation area, and the detoxified cyanide tailings need further care. The methods of backfilling [24] and reclamation of land [25] are also used for the disposal of CTs. However, high costs and strict environmental requirements may restrict their practical application [26].

Based on the content of valuable metals such as gold and silver in the CTs, various approaches on the recovery of Au and Ag [27,28] and the extraction of Fe, S, Pb-Zn, and Cu [29–32] have been proposed. To fully utilize the “low-value content” in the CTs, such as SiO\(_2\) and Al\(_2\)O\(_3\), some researchers have investigated the potential use of CTs for producing brick [33], glass-ceramics [34], aerated concrete [35], and Portland cement [36]. However, to the best of our knowledge, the technology on CSA cement clinker produced by pyrite-rich CTs has not been reported. In this work, the calcination process for the preparation of CSA cement clinker using pyrite-rich CTs was investigated to elucidate the calcination mechanism of pyrite-rich CTs to produce CSA cement clinker. The potential effect of operational parameters on the formation of CSA cement clinker and its compressive strength was examined in detail, including temperature and calcination time. The feasibility of recycling CTs as the cement material for mining infrastructure construction and backfilling is discussed.

2. Materials and Methods

2.1. Raw Materials

The pyrite-rich CTs used in this study were obtained from a gold mining company in Shandong Province of China. To eliminate the interference of impurities, the analytical reagents alumina and calcium carbonate, supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), were used to produce cement clinker. The pyrite-rich CTs were dehydrated at 60 °C for 72 h and crushed to below 58 µm in particle size. Calcium carbonate was calcined at 1050 °C for 240 min to prepare CaO as a raw material. The other chemical reagents (Shanghai, China) used in this work were of analytical grade.

2.2. Experimental Procedure

The main phases of ordinary CSA cement clinker are C\(_4\)A\(_3\)S\(_5\), 4CaO·Al\(_2\)O\(_3\)·Fe\(_2\)O\(_3\) (C\(_4\)AF), and 2CaO·SiO\(_2\) [2]. Therefore, the designed mineral composition of the cement clinker was C\(_4\)A\(_3\)S\(_5\), C\(_4\)AF, 2CaO·SiO\(_2\) (if any), and CaO·TiO\(_2\) (if any). About 5 g of CTs were weighed, and the proportion of CaO and Al\(_2\)O\(_3\) was determined by Equations (1) and (2) [37]. The alkalinity modulus (C\(_m\)) was 1.00, and the alumina–sulfur ratio (P) was 3.82. These raw materials were then uniformly mixed in a ball mill for 3 h. After homogenization, the mixture was cold isostatically pressed at 15 MPa to produce cylindrical samples with a diameter and height of 20 and 25 mm, respectively. The cylinders were calcined in a programmable resistance furnace (Shanghai, China) from room temperature to the setting temperature (900–1450 °C) at a heating rate of 10 °C min\(^{-1}\) in air. According to the literature [4], after calcining at the setting temperature for setting time, the cement clinker was taken out immediately and cooled.
down in air. The mixture and clinker were weighed and the values recorded. The cooled clinker was
ground to a particle size of less than 58 µm for the following analysis:

\[ C_m = \frac{(\text{CaO} - 0.7\text{TiO}_2)}{[1.87 \text{SiO}_2 + 0.73 (\text{Al}_2\text{O}_3 - 0.64\text{Fe}_2\text{O}_3) + 1.40\text{Fe}_2\text{O}_3]} \]  
\[ P = \frac{(\text{Al}_2\text{O}_3 - 0.64\text{Fe}_2\text{O}_3)}{\text{SO}_3} \]

2.3. Analysis

The chemical composition of CaO and S in the mixture and cement clinker were determined by
inductively coupled plasma optical emission spectroscopy (Agilent 7800, Agilent Technologies Inc.,
Santa Clara, CA, USA) and a carbon/sulfur analyzer (SC 114DR, LECO, St. Joseph County, MI, USA),
respectively. The free CaO (f-CaO) in the cement clinker was analyzed according to a Chinese standard
of GB/T 176-2008 [38]. The total cyanides in the CTs and cement clinker were analyzed according to a
Chinese standard of HJ 745-2015 [39].

The phase composition of the cement clinker was estimated using a PW 3040/60 (PANalytical,
Netherlands) with Cu-Kα radiation. The diffractometer was conducted at 45 kV and 40 mA with a
scanning rate of 5°·min⁻¹ and a range of 5°–80° (2θ). Each powdered sample was evenly placed onto a
rectangular steel holder, flattened with a glass slide. The data was analyzed by Jade 6.0 (MDI, USA)
using the PDF2-2004 database. The Rietveld quantitative analysis of the mineralogical composition
of the CSA cement clinker was determined by the internal standard method with 15.0% MgO addition.

The cement clinker was then mixed with 30% calcium sulfate dihydrate (analytical reagent) to
produce CSA cement. The cement slurry was prepared at a water-to-blinder ratio of 0.50. After stirring
for 4 min in a mechanical mixer (NJ-160, Huaxi Building Materials Testing Inc., Wuxi, Jiangsu, China),
the paste was filled into 20 × 20 × 20 mm³ steel molds and compacted. The fresh samples were covered
with a polyethylene sheet to prevent evaporation. Subsequently, the samples were demolded and
cured in water at 20 ± 1 °C [40]. Thereafter, the compressive strength of different hardened samples
with curing ages of 1, 3, and 28 days was measured using an HM-5030.3F (Humboldt, USA) at a speed
of 7 mm/min. Four specimens were tested for each condition.

2.4. Calculation

The mass ratio of the cement clinker to the mixture \( (w_{cm}) \) was determined based on the discrepancy
between the initial and remnant masses. The decomposition ratio of S in the mixture \( (\eta_S) \) was calculated
based on the chemical composition of S in the mixture and cement clinker.

\[ w_{cm} = \frac{m_c}{m_m} \times 100\% \]  
\[ \eta_S = \frac{(m_m \times w_m - m_c \times w_c)}{(m_m \times w_m)} \times 100\% \]

where

\( m_m \) is the mass of the mixture;

\( m_c \) is the mass of the cement clinker;

\( w_{cm} \) is the mass ratio of the cement clinker to the mixture;

\( w_m \) is the mass ratio of S in the mixture;

\( w_c \) is the mass ratio of S in the cement clinker.

3. Results and Discussion

3.1. Characterization of the Raw Materials

The chemical compositions of the pyrite-rich CTs, calcium carbonate, and alumina are listed in
Table 1. The mineral phases of the pyrite-rich CTs, analyzed by X-ray diffraction (XRD), are shown
in Figure 1a. According to Table 1 and Figure 1a, the main components of the CTs are pyrite (FeS$_2$), quartz (SiO$_2$) as well as minor muscovite with a total cyanide of 339 mg·kg$^{-1}$. Analysis of Al$_2$O$_3$ by X-ray diffraction (Figure 1b) reveals that the diffraction peaks of Al$_2$O$_3$ are poor, which is believed to be attributed to the amorphous state of Al$_2$O$_3$. The analytical reagent of calcium carbonate contains 55.91% CaO, whereas that of alumina mainly consists of 94.60% Al$_2$O$_3$ and 5.09% loss on ignition (LOI).

Table 1. Chemical composition of raw materials (wt %).

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Total Fe</th>
<th>S</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>LOI</th>
<th>Total Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide tailings</td>
<td>41.41</td>
<td>48.40</td>
<td>5.72</td>
<td>0.47</td>
<td>1.48</td>
<td>–</td>
<td>339.14 × 10$^{-6}$</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>55.91</td>
<td>0.01</td>
<td>43.88</td>
<td>–</td>
</tr>
<tr>
<td>Alumina</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
<td>94.60</td>
<td>5.09</td>
<td>–</td>
</tr>
</tbody>
</table>

Note: LOI, loss on ignition.

Figure 1. X-ray diffraction (XRD) pattern of (a) pyrite-rich cyanide tailings and (b) Al$_2$O$_3$.

3.2. Compressive Strength of the Cement Clinker

According to reaction (5), the phase of C$_4$A$_3$S in the cement clinker reacts rapidly with water (H) and CaSO$_4$·2H$_2$O (CS$_2$H$_2$) to form 3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O (AFt) and Al(OH)$_3$ (AH$_3$), which play important roles in the early-age strength development [4]. The calcination temperature and time directly affect the performance of cement clinker [2]. The influence of calcination temperature and calcination time on the compressive strength of the cement clinker was explored at 1250–1350 °C for 40–80 min. The compressive strength of the cement clinker calcined under various conditions at
different curing ages is shown in Figure 2, including that of CSA cement labeled with 42.5 grade (42.5 CSA) in Chinese standard GB/T 20472–2006.

![Figure 2](image-url)

**Figure 2.** Compressive strength of the cement clinker calcined (a) at 1250–1350 °C for 60 min and (b) at 1300 °C for 40–80 min.

Figure 2a shows that the compressive strength of the cement clinker increases with the increase in curing ages. When the calcination temperature rises from 1250 °C to 1300 °C, the compressive strength of the cement clinker at the same curing ages increases, but decreases dramatically as the temperature rises to 1350 °C. According to L. W. et al. [41], it is believed that C₄A₃S is not formed completely at low temperature, and the crystal particle of C₄A₃S is larger at high temperature, leading to the deterioration of the cement clinker’s activity. The compressive strength of the cement clinker calcined at 1300 °C is similar to that of 42.5 CSA. This suggests that the optimal calcination temperature is determined to be 1300 °C and the compressive strength of the cement clinker meets the requirements of 42.5 CSA. In Figure 2b, the compressive strength of the cement clinker increases with the increase in curing ages. With the prolongation of calcination time, the compressive strength of the cement clinker decreases at the curing ages of 1 and 3 days, but remains almost constant first and then decreases at the curing age of 28 days. This suggests that the cement clinker’s activity decreases with the extension of calcination time. The compressive strength of the cement clinker calcined at 1300 °C for 40–60 min meets the requirements of 42.5 CSA. This suggests that the cement clinker meeting the compressive strength requirements of 42.5 CSA can be obtained at 1300 °C for 40–60 min.

\[
\text{C}_4\text{A}_3\text{S} + 2 \text{C}_\text{S}\text{H}_2 + 34 \text{ H} \rightarrow \text{AFt} + 2 \text{ AH}_3
\]  

(5)
3.3. Behavior of Pyrite in CTs During Calcination

To investigate the behavior of pyrite in CTs during the production of CSA cement clinker, a series of experiments were conducted at 900–1300 °C without retention time. Cyanides were not detected in all samples. According to the results of previous research [42], it is believed that the cyanides in CTs decompose into carbonate, CO$_2$, and N$_2$ during the calcination process. The other results are displayed in Figure 3. As shown in Figure 3a, $w_{\text{c/m}}$ is more than 100% in all cases and decreases slightly with increasing temperature, indicating that during the calcination process the pyrite in CTs is oxidized [43]. The increase of $\eta_S$ with increasing temperature suggests that some of the formed sulfur-containing components decompose at higher temperatures. The mass ratio of f-CaO in the samples decreases with the increase in temperature, indicating that more and more f-CaO is involved in the formation of cement clinker. When the mixture calcined at 1300 °C without retention time, 4% of f-CaO was detected in the sample, indicating that the reaction between f-CaO and the pyrite-rich CTs is still incomplete [6].

![Figure 3](image-url)

**Figure 3.** (a) Variation of the mass of the cement clinker to the mixture ($w_{\text{c/m}}$), the decomposition ratio of S for the mixture ($\eta_S$), and the mass ratio of free CaO (f-CaO) in the cement clinker versus temperature at 900–1300 °C without retention time; (b) XRD patterns of the cement clinker calcined at 1000–1300 °C without retention time.

Figure 3b shows that the phase composition of the clinker varies greatly at different temperatures. The diffraction peaks of Al$_2$O$_3$ are absent in all samples as it is amorphous. The sample calcined at 1000 °C consists of Fe$_2$O$_3$, CaSO$_4$, and f-CaO, suggesting that FeS$_2$ reacts with O$_2$ and f-CaO to form Fe$_2$O$_3$ and CaSO$_4$ by reactions (6) and (7). New phases of CaO·2Al$_2$O$_3$ (C$_2$A) and 2CaO·Fe$_2$O$_3$ (C$_2$F) are presented at 1100 °C, indicating that reactions (8) and (9) occur at 1100 °C, C$_4$A$_3$S and 12CaO·7Al$_2$O$_3$ (C$_{12}$A$_7$) are observed at 1150 °C, and the diffraction intensity of Ca$_2$ and CaSO$_4$ decreases rapidly.
over 1150 °C. This suggests that the reactions (10)–(12) occur over 1150 °C. When the mixture calcines at 1250 or 1300 °C, the clinker is composed of $\text{C}_4\text{A}_3\text{S}$, $\text{C}_4\text{AF}$, $\text{CA}_2$, $\text{C}_{12}\text{A}_7$, and $\text{C}_2\text{F}$. As the calcination temperature increases, the diffraction intensity of $\text{Fe}_2\text{O}_3$ and $\text{CaSO}_4$ gradually decreases but disappears at 1250 °C, whereas that of $\text{f-CaO}$ decreases sharply. This suggests that reactions (9)–(11) are almost complete. The diffraction intensity of $\text{CA}_2$ increases first and then decreases, whereas that of $\text{C}_4\text{A}_3\text{S}$ and $\text{C}_{12}\text{A}_7$ increases substantially with increasing temperature, meaning that $\text{CA}_2$ is formed as an intermediate, and the increase in temperature facilitates the reactions (8) and (10)–(12). The diffraction intensity of $\text{C}_2\text{F}$ decreases gradually and nearly disappears, whereas that of $\text{C}_4\text{AF}$ remains almost constant above 1250 °C. It suggests that $\text{C}_2\text{F}$ is also formed as an intermediate, and higher temperatures promote reactions (13) and (14).

3.4. Preparation of the Cement Clinker

3.4.1. Effect of Calcination Temperature

The effect of calcination temperature on the preparation of the cement clinker was investigated by maintaining the mixture at 1200–1450 °C for 60 min. The results (Figure 4a) show that $\eta_S$ is more than 100% in all cases and gradually decreases with the increase in temperature. This indicates that the oxidation of pyrite-rich CTs increases the mass of cement clinker. The increase of $\eta_S$ with the rise in temperature indicates that higher temperatures promote the loss of sulfur in clinker. The mass ratio of $\text{f-CaO}$ in clinker decreases rapidly with the rise in temperature, suggesting that higher temperatures facilitate the reactions in which $\text{f-CaO}$ is consumed.

3.4.2. Effect of Calcination Time

The effect of calcination time on the preparation of the cement clinker was explored at 1300 °C for 0–80 min. The results presented in Figure 4b show that $\eta_S$ increases gradually, whereas the mass ratio of $\text{f-CaO}$ decreases rapidly with the prolongation of reaction time. The mass ratio of $\text{f-CaO}$ is undetected as the calcination time is above 40 min. This suggests that longer calcination time contributes to the loss of sulfur and the consumption of $\text{f-CaO}$ in clinker, and favors reactions (13) and (14).
meaning that CA\(_2\) is formed as an intermediate, and the increase in temperature facilitates the reactions (8) and (10)–(12). The diffraction intensity of C\(_2\)F decreases gradually and nearly disappears, whereas that of C\(_4\)AF remains almost constant above 1250 °C. It suggests that C\(_2\)F is also formed as an intermediate, and higher temperatures promote reactions (13) and (14).

\[
\begin{align*}
2\text{FeS} + 11\text{O}_2 &\rightarrow \text{Fe}_2\text{O}_3 + 8\text{SO}_2 \\
2\text{CaO} + 2\text{SO}_2 + \text{O}_2 &\rightarrow 2\text{CaSO}_4 \\
2\text{CaO} + 2\text{Al}_2\text{O}_3 &\rightarrow \text{CaO} + 2\text{Al}_2\text{O}_3 \\
2\text{CaO} + 2\text{Fe}_2\text{O}_3 &\rightarrow 2\text{CaO} + 2\text{Fe}_2\text{O}_3 \\
2\text{CaO} + 3\text{Al}_2\text{O}_3 + \text{CaSO}_4 &\rightarrow 3\text{CaO} + 3\text{Al}_2\text{O}_3 + \text{CaSO}_4 \\
2\text{CaO} + 7\text{Al}_2\text{O}_3 &\rightarrow 2\text{CaO} + 7\text{Al}_2\text{O}_3 \\
2\text{CaO} + 2\text{Al}_2\text{O}_3 + 2\text{Fe}_2\text{O}_3 &\rightarrow 2\text{CaO} + 2\text{Al}_2\text{O}_3 + 2\text{Fe}_2\text{O}_3 \\
\end{align*}
\]

3.4. Preparation of the Cement Clinker

3.4.1. Effect of Calcination Temperature

Figure 4. Variation of the mass of the cement clinker to the mixture (\(w_{\text{c/m}}\)), the decomposition ratio of S for the mixture (\(\eta_S\)), and the mass ratio of free CaO (f-CaO) in the cement clinker versus (a) temperature at 1200–1450 °C for 60 min and (b) calcination time at 1300 °C for 0–80 min.

3.5. Mineral Phases of the Cement Clinker

3.5.1. XRD Patterns at Different Calcination Temperatures

The XRD patterns of the cement clinker calcined at 1250–1400 °C for 60 min are shown in Figure 5a. It shows that C\(_4\)A\(_3\)S, C\(_4\)AF, and C\(_{12}\)A\(_7\), which are favorable phases in normal CSA cement clinker [44], occur at all cement clinker phases. CA\(_2\) and C\(_2\)F are found in the clinker calcined at 1250 °C for 60 min. The major phases of the cement clinker calcined above 1300 °C for 60 min are C\(_4\)A\(_3\)S, C\(_4\)AF, and C\(_{12}\)A\(_7\), suggesting that a higher temperature favors the decomposition of intermediates (CA\(_2\) and C\(_2\)F) and the formation of the desired mineral phases of CSA cement. The mineralogical composition of the cement clinker was analyzed using the Rietveld refinement method with 15.0% MgO internal standard. The portable document format (PDF) and inorganic crystal structure database (ICSD) codes of mineral phases for quantitative analysis are listed in Table 2, and the refinement results are listed in Table 3.

When the mixture calcined at 1250 °C for 60 min, 1.9% C\(_2\)F and 5.2% CA\(_2\) remain in clinker, while 61.2% C\(_4\)A\(_3\)S and 7.4% C\(_4\)AF are formed. C\(_2\)F and CA\(_2\) disappear at higher temperatures, indicating that reaction (14) happens. The content of C\(_4\)A\(_3\)S increases with the rise in temperature, while that of C\(_4\)AF increases considerably, and that of C\(_{12}\)A\(_7\) decreases. This demonstrates that a higher temperature promotes the formation of C\(_4\)A\(_3\)S and C\(_4\)AF, but causes the decomposition of C\(_{12}\)A\(_7\).
Figure 5. XRD patterns of the cement clinker calcined (a) at 1250–1400 °C for 60 min and (b) at 1300 °C for 0–80 min.

Table 2. The portable document format (PDF) and the inorganic crystal structure database (ICSD) codes of mineral phases used for Rietveld refinement.

<table>
<thead>
<tr>
<th>Mineral Phases</th>
<th>PDF Code</th>
<th>ICSD Code</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>C₄A₃S</td>
<td>85-2210</td>
<td>80361</td>
<td>[45]</td>
</tr>
<tr>
<td>C₄AF</td>
<td>74-1346</td>
<td>27112</td>
<td>[46]</td>
</tr>
<tr>
<td>C₁₂A₇</td>
<td>70-2144</td>
<td>6287</td>
<td>[47]</td>
</tr>
<tr>
<td>C₂F</td>
<td>71-2264</td>
<td>15059</td>
<td>[48]</td>
</tr>
<tr>
<td>CA₂</td>
<td>89-3851</td>
<td>44519</td>
<td>[49]</td>
</tr>
<tr>
<td>f-CaO</td>
<td>78-0649</td>
<td>61550</td>
<td>[50]</td>
</tr>
<tr>
<td>MgO</td>
<td>78-0430</td>
<td>61325</td>
<td>[51]</td>
</tr>
</tbody>
</table>

Table 3. Mineralogical composition of the cement clinker calcined at 1250–1400 °C for 60 min by Rietveld refinement with 15.0% MgO internal standard (wt %).

<table>
<thead>
<tr>
<th>T/°C</th>
<th>C₄A₃S</th>
<th>C₄AF</th>
<th>C₁₂A₇</th>
<th>C₂F</th>
<th>CA₂</th>
<th>MgO</th>
<th>R</th>
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<tr>
<td>1250</td>
<td>61.2</td>
<td>7.4</td>
<td>9.3</td>
<td>1.9</td>
<td>5.2</td>
<td>14.9</td>
<td>8.96</td>
</tr>
<tr>
<td>1300</td>
<td>64.1</td>
<td>11.0</td>
<td>9.4</td>
<td>–</td>
<td>–</td>
<td>15.3</td>
<td>8.08</td>
</tr>
<tr>
<td>1350</td>
<td>65.6</td>
<td>12.4</td>
<td>7.1</td>
<td>–</td>
<td>–</td>
<td>14.9</td>
<td>8.14</td>
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<tr>
<td>1400</td>
<td>68.8</td>
<td>13.5</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
<td>14.8</td>
<td>9.21</td>
</tr>
</tbody>
</table>

Note: R, weighted residual error of refinement.
3.5.2. XRD Patterns at Different Calcination Times

The cement clinker calcined at 1300 °C for 0–80 min was analyzed by XRD. As shown in Figure 5b, C₄Å₃S, C₄AF, and C₁₂A₇ are present in all cement clinker phases. F-CaO is observed at the free retention time of 1300 °C, but disappears when the calcination time exceeds 20 min, indicating that part of f-CaO remains unreacted due to the lack of calcination time, and the reactions involving the consumption of f-CaO are almost complete when the calcination time exceeds 20 min. CA₂ and C₂F are found in the clinker calcined at 1300 °C for 0–40 min, but disappear when the calcination time is above 40 min. The major phases of the cement clinker calcined at 1300 °C for more than 40 min are C₄Å₃S, C₄AF, and C₁₂A₇. This indicates that the prolongation of calcination time contributes to the decomposition of CA₂ and C₂F and the formation of the desired mineral phases of C₄Å₃S and C₄AF.

The mineralogical composition of the cement clinker was analyzed using the Rietveld refinement method with 15.0% MgO internal standard. The PDF and ICSD codes of mineral phases for quantitative analysis are listed in Table 2, and the results are listed in Table 4. The clinker contains 56.7% C₄Å₃S, 7.5% C₄AF, and 9.3% C₁₂A₇, as well as 3.1% C₂F, 4.7% CA₂, and 3.3% f-CaO when the mixture calcined at 1300 °C without retention time. It implies that the reactions in cement clinker are not complete due to the lack of reaction time. F-CaO was not found at 1300 °C for 20 min, corresponding to the results shown in Figure 4b. This indicates that the reactions involving f-CaO are complete. C₂F and CA₂ are absent in the cement clinker calcined at 1300 °C for more than 40 min. The content of both C₄Å₃S and C₄AF increases significantly with calcination time, whereas that of C₁₂A₇ remains quite constant. This suggests that the prolongation of the calcination time promotes the decomposition of CA₂ and C₂F and the formation of C₄Å₃S and C₄AF. Overall, the favorable cement clinker is obtained at 1300 °C for more than 40 min.

<table>
<thead>
<tr>
<th>t/min</th>
<th>C₄Å₃S (wt %)</th>
<th>C₄AF</th>
<th>C₁₂A₇</th>
<th>C₂F</th>
<th>CA₂</th>
<th>CaO</th>
<th>MgO</th>
<th>R</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>56.7</td>
<td>7.5</td>
<td>9.3</td>
<td>3.1</td>
<td>4.7</td>
<td>3.3</td>
<td>15.4</td>
<td>8.99</td>
</tr>
<tr>
<td>20</td>
<td>62.1</td>
<td>7.5</td>
<td>9.7</td>
<td>2.3</td>
<td>3.6</td>
<td>–</td>
<td>14.9</td>
<td>9.30</td>
</tr>
<tr>
<td>40</td>
<td>64.1</td>
<td>7.0</td>
<td>9.1</td>
<td>2.3</td>
<td>2.4</td>
<td>–</td>
<td>15.1</td>
<td>9.09</td>
</tr>
<tr>
<td>60</td>
<td>64.1</td>
<td>11.0</td>
<td>9.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.3</td>
<td>8.08</td>
</tr>
<tr>
<td>80</td>
<td>64.4</td>
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<td>9.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.3</td>
<td>8.72</td>
</tr>
</tbody>
</table>

Note: R, weighted residual error of refinement.

4. Conclusions

It is feasible to produce CSA cement clinker using pyrite-rich CTs as the sources of Fe₂O₃ and SO₃. The main conclusions are summarized as follows.

The compressive strength of cement clinker is affected by calcination temperature and time, especially the calcination temperature. It meets the compressive strength criteria of 42.5 CSA when the mixture is calcined at 1300 °C for 40–60 min.

During the calcination process, the cyanides decompose into carbonate, CO₂, and N₂. The pyrite is oxidized into Fe₂O₃ and SO₂ below 1000 °C and they react with CaO and Al₂O₃ above 1000 °C to form the intermediates of CaSO₄, CF₂, and CA₂, which further react to form the desired mineral phases of C₄Å₃S and C₄AF.

In the production of CSA cement clinker, the mass ratio of f-CaO and the decomposition of S in CSA cement clinker are influenced by calcination temperature and time. The optimal conditions are to calcine the mixture at 1300 °C for 40–60 min.

The major mineral phases of the cement clinker calcined at 1300 °C for more than 40 min are C₄Å₃S, C₄AF, and C₁₂A₇.
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