

Article

Characteristics of Solid Mineral Phase Transitions During Sulfuric Acid Production from Gaseous-Sulphur-Reduced Gypsum

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Abstract: The acid co-production of cement is a prominent research focus for the large-scale, high-value utilization of phosphogypsum in the context of dual-carbon strategies. This paper builds on extensive research conducted by its authors on the co-production of sulfoaluminate cement clinker through acid production from gaseous-sulphur-reduced phosphogypsum. The solid mineral phase transformations occurring in the kiln during this process are systematically studied, and the effects of various calcination regimes (temperature, time, and atmosphere) on the evolution of clinker mineral phases are elucidated. This paper provides basic data support for the gas-sulfur-reduced phosphogypsum-acid cogeneration of sulfoaluminate cement clinker processes, and promotes the realization of the large-scale high-value utilization of phosphogypsum resources. The generation of the clinker mineral phase anhydrous calcium sulfoaluminate ($C_4A_3\bar{S}$) begins at 1100 °C. Increasing the calcination temperature and extending the calcination time promote $C_4A_3\bar{S}$ formation. However, when the calcination temperature exceeds 1350 °C, $C_4A_3\bar{S}$ decomposes, leading to the formation of low-activity C_2AS . In a CO atmosphere, the main mineral phases in the clinker transform into C_2AS and $12CaO \cdot 7Al_2O_3$, owing to the decomposition of $CaSO_4$, which inhibits $C_4A_3\bar{S}$ formation. At calcination temperatures exceeding 1300 °C, a significant amount of C_2AS appears in the calcined material, and $12CaO \cdot 7Al_2O_3$ begins to form.



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Keywords: phosphogypsum; gaseous sulphur; mineral phase evolution; sulfoaluminate cement clinker

1. Introduction

Phosphogypsum is an industrial by-product generated during the wet production of phosphoric acid in the phosphorus chemical industry. For every ton of phosphoric acid produced, 4 to 5 tons of phosphogypsum are generated [1–4]. Reducing phosphogypsum through sulphur reduction for the co-production of sulfoaluminate cement clinker is an effective resource-utilization method, addressing the issue of large phosphogypsum accumulation [5]. The CaO produced by the partial decomposition of phosphogypsum serves as a calcium source in the clinker formation reaction, while the remaining portion is directly involved in the formation of anhydrous calcium sulfoaluminate ($C_4A_3\bar{S}$) in the cement clinker [6–9].

To effectively reduce the environmental impact of phosphogypsum, and to ensure the high-value utilization of phosphogypsum resources, the use of coke reduction for the preparation of sulfoaluminate cement clinker has been initially proposed, and considerable research has been conducted on this approach [10–13]. However, coke reduction has several drawbacks, including a high decomposition temperature, low SO_2 concentration, and high energy consumption [14–16]. To address these limitations, sulphur was chosen as the reducing agent and an in-depth study was conducted on the process of sulphur reduction for both acid production and the co-production of sulfoaluminate cement clinker [17,18]. The Institute of Powder Engineering at Xi'an University of Architecture and

Technology conducted a pilot test using dilute-phase suspension roasting technology for the reduction of phosphogypsum to produce acid and cement [19]. Relevant test results have proven the applicability of the gas sulfur reduction of phosphogypsum to the acid cogeneration of sulfoaluminate cement clinker, which can substantially increase the phosphogypsum consumption, and at the same time has a very considerable economic value. During this group's research on this process, it was discovered that the clinker composition contained a significant amount of the inert mineral calcium–aluminum yellow feldspar (C_2AS). Therefore, understanding the formation mechanism of C_2AS is crucial. To further investigate the formation of the clinker mineral phases $C_4A_3\bar{S}$ and C_2AS , raw material configurations were simulated and fed into a rotary kiln to study the solid-phase formation mechanisms and transformation characteristics.

This paper investigates the influence of various calcination regimes (temperature, time, and atmosphere) on the formation of clinker mineral phases. It examines the transformation patterns between different clinker mineral phases and identifies the main factors affecting these transformations. The goal is to determine the optimal control range for each process parameter in the co-production of sulfoaluminate cement clinker and acid from gaseous-sulphur-reduced phosphogypsum.

2. Materials and Methods

2.1. Materials and Experimental Methods

Gas sulfur reduction of phosphogypsum to make acid co-production of sulfoaluminate cement clinker is an effective method to solve the problem of large amounts of phosphogypsum stockpiling. The process flow diagram for the co-production of sulfoaluminate cement and acid from gaseous-sulphur-reduced phosphogypsum is illustrated in Figure 1a, with the pilot test site illustrated in Figure 1b. The process consists of two phases: (1) a preheating and pre-decomposition phase and (2) a secondary decomposition phase in the kiln. The material, composed of phosphogypsum and other silica–aluminum raw materials mixed in a specific proportion, is fed into the suspension preheater through a feeder. After heat exchange with high-temperature flue gas in the preheater, the material enters the reduction furnace, where it undergoes a redox reaction with high-temperature sulphur vapor, before entering the kiln for the clinker sintering reaction.

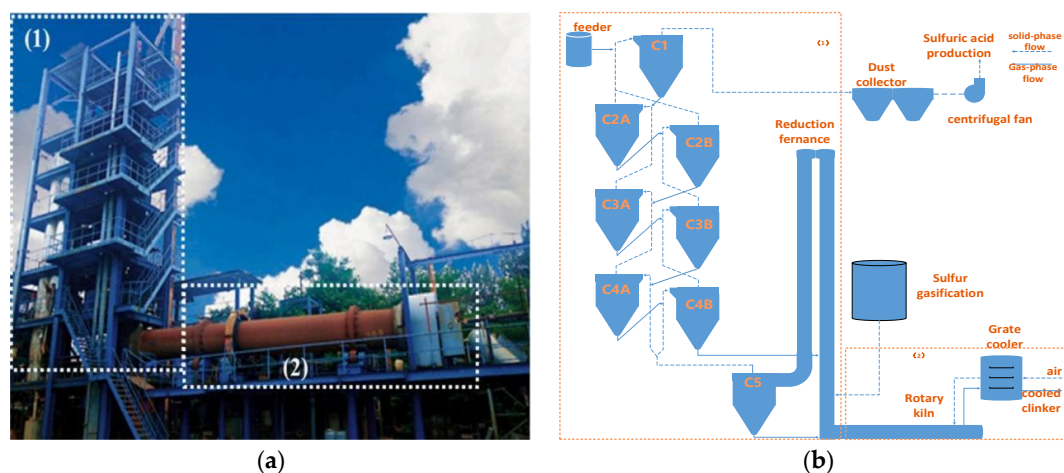


Figure 1. Preparation of sulfoaluminate cement from gaseous-sulphur-reduced phosphogypsum: (a) pilot site diagram; (b) process flow diagram.

Analytically pure CaS , $CaSO_4 \cdot 2H_2O$, SiO_2 , and Al_2O_3 were used as raw materials (concentration greater than 99.7%). The aim was to exclude the influence of impurities in phosphogypsum on the experimental results. The raw materials were mixed with 10% anhydrous ethanol and then pressed into $\Phi 12 \text{ mm} \times 10 \text{ mm}$ specimens. The pressed specimens were placed in a drying oven at 120°C and dried to a constant weight. The

main components of the prepared raw materials, as measured via X-ray diffraction (XRD), are illustrated in Figure 2.

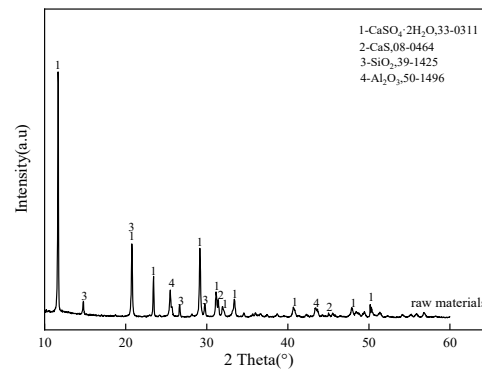
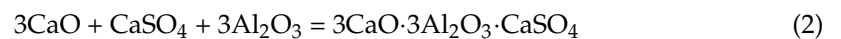


Figure 2. XRD pattern of the raw materials.

The theoretical clinker composition was determined as 60% $C_4A_3\bar{S}$ and 40% C_2S , and the required amounts of raw materials were calculated to meet this composition. Some of the $CaSO_4$ and CaS initially underwent a complex decomposition reaction to form CaO , while the remaining $CaSO_4$ participated in the formation of the $C_4A_3\bar{S}$ mineral phase of the cement clinker, acting as externally mixed gypsum. It is assumed that the clinker firing reaction at high temperatures follows Equations (1) and (2):



The raw material ratios and theoretical clinker compositions are shown in Table 1.

Table 1. Raw material ratio and theoretical clinker composition.

	CaS	CaSO ₄	SiO ₂	Al ₂ O ₃	$C_4A_3\bar{S}$	C_2S
Molar mass	72	136	60	102	610	172
Raw material ratio/wt%	9.2	61.2	9.4	20.2	60	40

The calcination regimes used for the tests included the following: calcination temperatures of 1000 °C–1400 °C, calcination times of 15 min–60 min, and various atmospheres (1% to 3% O₂, N₂, or 1% to 3% CO). After pressing, the test blocks were placed in a tube furnace where different calcination regimes were applied to study the evolution of the main mineral phases $C_4A_3\bar{S}$, C_2AS , and C_2S in the clinker. The cement clinker was then removed from the tube furnace and allowed to cool. Figure 3 illustrates the flow chart of this experiment.

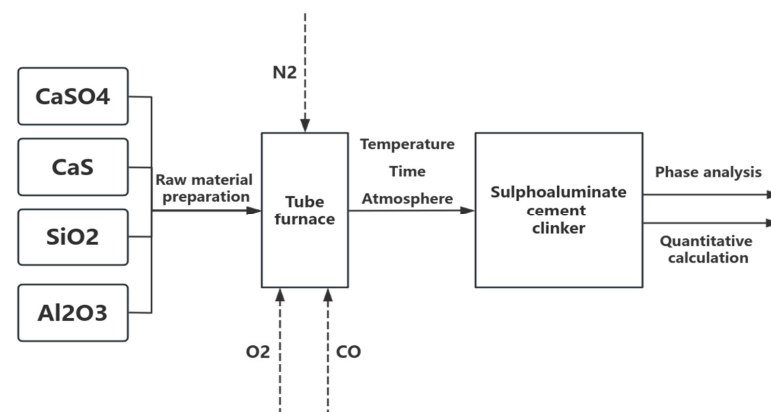


Figure 3. Experiment flow diagram.

2.2. Material Characterization

The sulphide content was determined using the iodometric method specified in GB/T 176-2008 Methods of Chemical Analysis of Cement to determine the CaS content [20]. The mineral phase composition of the clinker was analyzed with a Bruker D8 Advance XRD instrument, using a test angle range of 20° to 60° (2θ), a scanning step of 0.02° , and a scanning speed of $2^\circ/\text{min}$. The structural composition and functional groups of the sulphaaluminate cement substances were examined with a Thermo Scientific Nicolet iS5 Fourier-transform infrared (FTIR) spectrometer, USA. The test range was $400\text{--}1400\text{ cm}^{-1}$. A Zeiss Sigma 300 scanning electron microscope was used to observe the microscopic morphology of the cement clinker samples. Quantitative analysis of the clinker mineral phases $\text{C}_4\text{A}_3\bar{\text{S}}$, C_2S , and C_2AS was conducted using the K-value method [21,22]. The strongest peaks of each mineral phase were selected for quantification, with K-values determined using Jade 6.5 software, as follows: $K_{\text{CaSO}_4} = 1.75$, $K_{\text{CaS}} = 6.05$, $K_{\text{CaO}} = 2.54$, $K_{\text{C}_4\text{A}_3\bar{\text{S}}} = 1.02$, $K_{\text{C}_2\text{S}} = 0.73$, and $K_{\text{C}_2\text{AS}} = 2.44$.

3. Results and Discussion

3.1. Effect of Calcination Temperature on the Evolution of Main Mineral Phases in Clinker

Figure 4 illustrates the XRD patterns of the materials calcined at different temperatures under a N_2 atmosphere and the corresponding trends in the content of each substance with respect to the calcination temperature. As illustrated in Figure 3, under a nitrogen atmosphere, increasing the calcination temperature causes CaSO_4 and CaS to initially undergo a complex decomposition reaction, producing CaO . This CaO then reacts further with CaSO_4 and Al_2O_3 to form $\text{C}_4\text{A}_3\bar{\text{S}}$ [8]. With increasing calcination temperature, the content of C_2S in the calcined material also increases. The chemical reaction equations involved are shown in Equations (3)–(5).

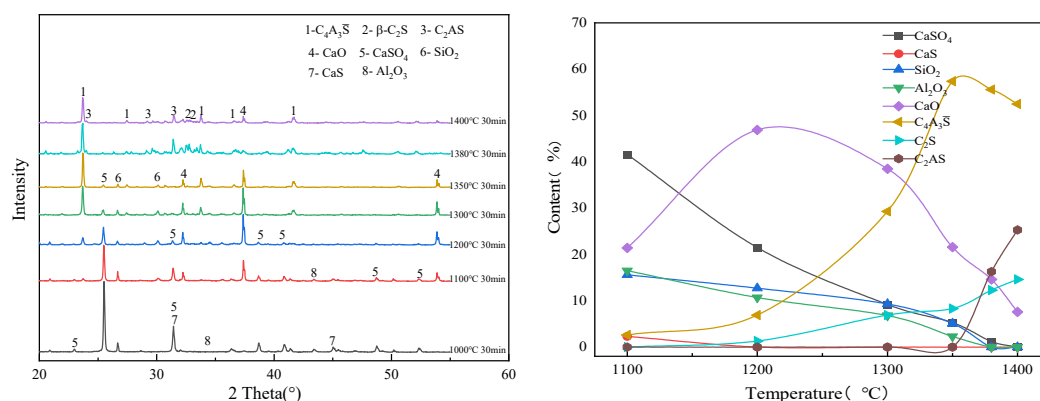
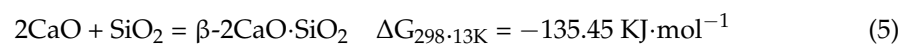
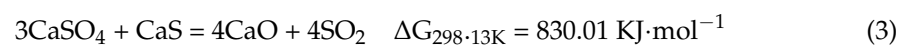


Figure 4. XRD patterns of materials calcined at different temperatures under N_2 atmosphere and the trend of each substance's content as a function of temperature.

The characteristic diffraction peaks of $\text{C}_4\text{A}_3\bar{\text{S}}$ begin to appear in the spectra of the material calcined at 1100°C after 30 min. The intensity of these diffraction peaks increases with rising calcination temperature, reaching its maximum at 1350°C . This indicates that $\text{C}_4\text{A}_3\bar{\text{S}}$ starts to form when the calcination temperature reaches 1100°C . Between 1100°C and 1350°C , the intensity of the diffraction peaks for $\text{C}_4\text{A}_3\bar{\text{S}}$ increases with higher temperatures, suggesting that a higher calcination temperature is favorable for the formation of the $\text{C}_4\text{A}_3\bar{\text{S}}$ mineral phase in the clinker. The intensity of the diffraction peak for $\text{C}_4\text{A}_3\bar{\text{S}}$ reaches its

maximum at 1350 °C. When the calcination temperature exceeds 1350 °C, the characteristic diffraction peak for C_2AS appears in the calcined material, indicating that $C_4A_3\bar{S}$ begins to decompose into the less active C_2AS . Consequently, the intensity of the diffraction peak for $C_4A_3\bar{S}$ decreases with further increases in calcination temperature [22]. The transformation of the clinker mineral phases with respect to the calcination temperature under a N_2 atmosphere is presented in Table 2, from which the generation and transformation temperatures of each clinker mineral phase can be seen.

Table 2. The transformation of clinker mineral phases with respect to the calcination temperature under N_2 atmosphere.

Temperature	Clinker Mineral Phase
1000 °C	$CaSO_4$, CaS , SiO_2 , Al_2O_3
1100 °C	$C_4A_3\bar{S}$, $CaSO_4$, CaS , SiO_2 , Al_2O_3 , CaO
1200 °C	$C_4A_3\bar{S}$, $CaSO_4$, SiO_2 , CaO , C_2S
1300 °C	$C_4A_3\bar{S}$, $CaSO_4$, SiO_2 , CaO , C_2S
1350 °C	$C_4A_3\bar{S}$, $CaSO_4$, SiO_2 , CaO , C_2S
1380 °C	$C_4A_3\bar{S}$, C_2S , C_2AS , CaO
1400 °C	$C_4A_3\bar{S}$, C_2S , C_2AS , CaO

Figures 5–7 illustrate the XRD patterns of the materials calcined at different temperatures under 1% O_2 , 2% O_2 , and 3% O_2 atmospheres, respectively. The figures also include corresponding trend plots showing the changes in the content of each substance with calcination temperature. The characteristic diffraction peaks of $C_4A_3\bar{S}$ begin to appear in the spectra of the material calcined at 1100 °C after 30 min, and the contents of both $C_4A_3\bar{S}$ and C_2S increase with higher calcination temperatures. When the calcination temperature exceeds 1350 °C, the characteristic diffraction peaks of C_2AS appear in the calcined material, while the intensity of the diffraction peaks for $C_4A_3\bar{S}$ gradually decreases with increasing temperature. This indicates that excessively high calcination temperatures lead to the decomposition of $C_4A_3\bar{S}$, the primary mineral phase of clinker, and the formation of the less active C_2AS . The presence of C_2AS in clinker can adversely affect its quality and reduce its hydration activity [23].

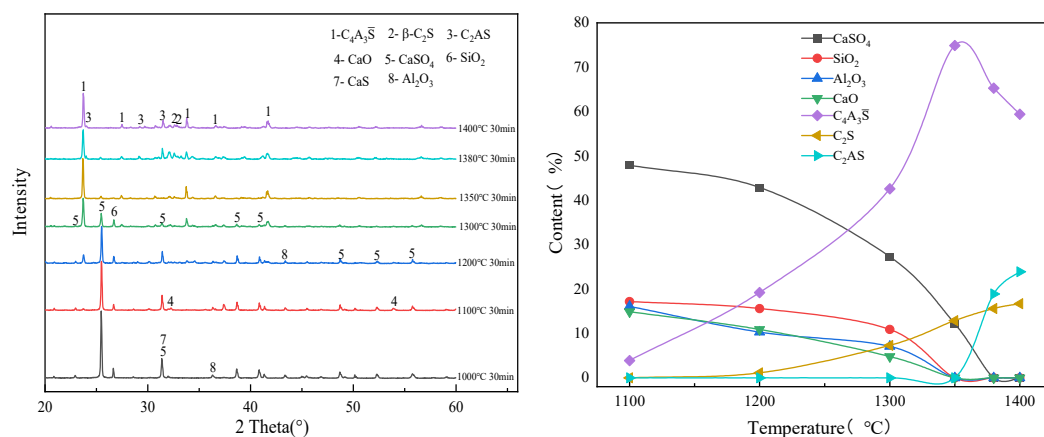


Figure 5. XRD patterns of materials calcined at different temperatures under 1% O_2 atmosphere, and the trend of each substance's content as a function of temperature.

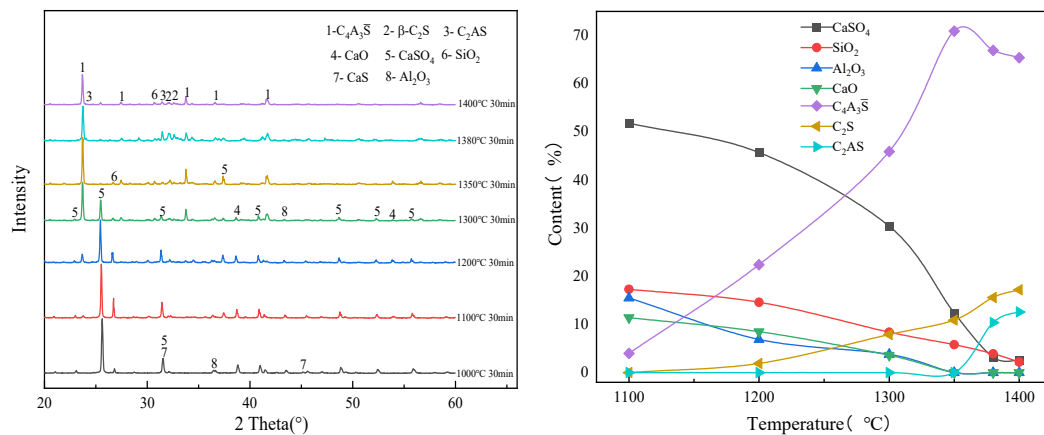


Figure 6. XRD patterns of materials calcined at different temperatures under 2% O₂ atmosphere, and the trend of each substance's content as a function of temperature.

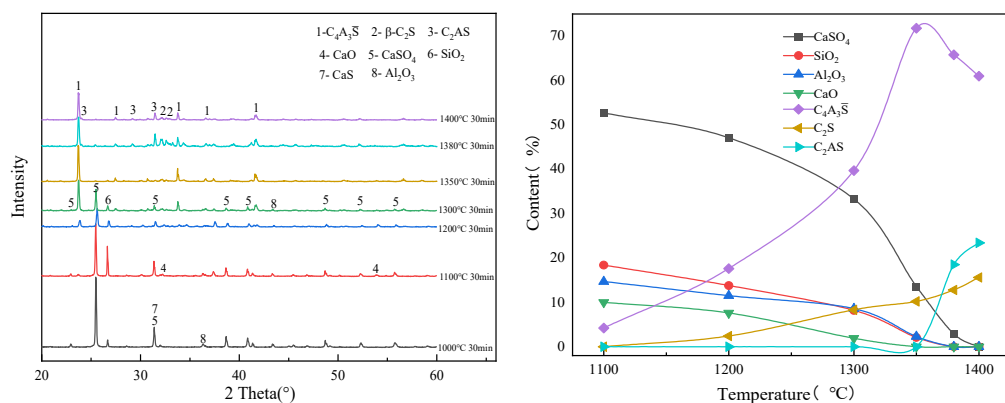


Figure 7. XRD patterns of materials calcined at different temperatures under 3% O₂ atmosphere, and the trend of each substance's content as a function of temperature.

In summary, under the oxidizing atmosphere, C₄A₃S̄ first appears in the material calcined at 1100 °C, and its content increases with rising calcination temperature. Once the calcination temperature reaches 1350 °C, the clinker mineral phase generation reaction is essentially complete. The transformation of clinker mineral phases with respect to the calcination temperature under an O₂ atmosphere is presented in Table 3, from which the generation and transformation temperatures of each clinker mineral phase can be seen. From the table, the generation and transformation temperatures of each clinker mineral phase can be visualized. When the calcination temperature reaches 1350 °C, the generation reaction of the clinker mineral phase occurs completely, and only the main mineral phase remains in the clinker, as C₄A₃S̄, C₂S, and C₂AS.

Table 3. The transformation of clinker mineral phases with respect to the calcination temperature under O₂ atmosphere.

Temperature	Clinker Mineral Phase
1000 °C	CaSO ₄ , CaS, SiO ₂ , Al ₂ O ₃
1100 °C	C ₄ A ₃ S̄, CaSO ₄ , CaS, SiO ₂ , Al ₂ O ₃ , CaO
1200 °C	C ₄ A ₃ S̄, CaSO ₄ , SiO ₂ , CaO, C ₂ S
1300 °C	C ₄ A ₃ S̄, CaSO ₄ , SiO ₂ , CaO, C ₂ S
1350 °C	C ₄ A ₃ S̄, C ₂ S, C ₂ AS
1380 °C	C ₄ A ₃ S̄, C ₂ S, C ₂ AS
1400 °C	C ₄ A ₃ S̄, C ₂ S, C ₂ AS

Figures 8–10 illustrate the XRD patterns of materials calcined at different temperatures under 1% CO, 2% CO, and 3% CO atmospheres, respectively, along with the corresponding trend plots showing the content of each substance as a function of temperature. Similarly to the trends under nitrogen and oxidizing atmospheres, the intensity of the diffraction peaks for $C_4A_3\bar{S}$ and C_2S in the calcined material increases with rising calcination temperature. The characteristic diffraction peaks of $C_4A_3\bar{S}$ begin to appear in the material calcined at 1100 °C after 30 min, and the intensity of these peaks increases with rising calcination temperature. However, under a reducing atmosphere, after the calcination temperature exceeds 1300 °C, a significant amount of C_2AS appears in the calcined material, indicating a shift in the main mineral phase composition to C_2AS . This suggests that a reducing atmosphere promotes the formation of the inert mineral phase, C_2AS . Additionally, the characteristic diffraction peak of $12CaO \cdot 7Al_2O_3$ appears in the calcined material, and its intensity increases with the strengthening of the CO atmosphere. The intensity of the diffraction peaks for C_2S is also higher than those of the peaks for C_2S subjected to nitrogen atmosphere and oxygen-poor conditions. This difference is due to the reaction between CaO, generated from the decomposition of $C_4A_3\bar{S}$, and free SiO_2 , which produces C_2S . Consequently, the C_2S content in the calcined material increases with higher calcination temperatures.

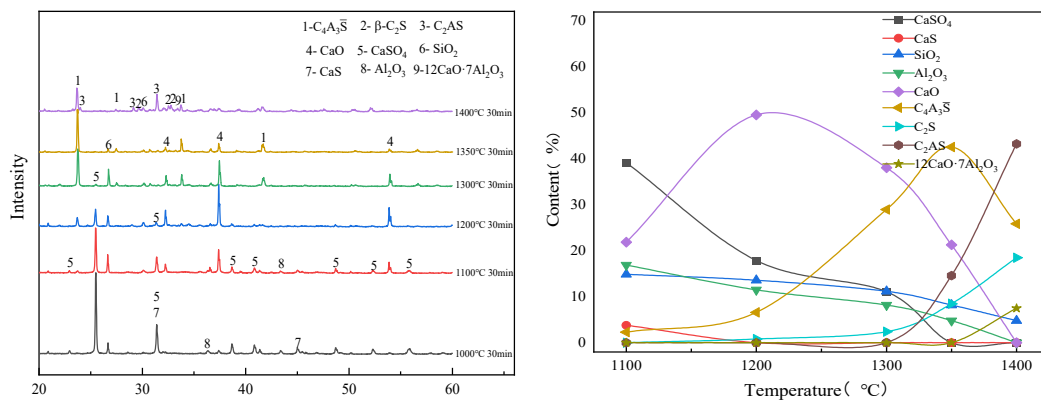


Figure 8. XRD patterns of materials calcined at different temperatures under 1% CO atmosphere, and the trend of each substance's content as a function of temperature.

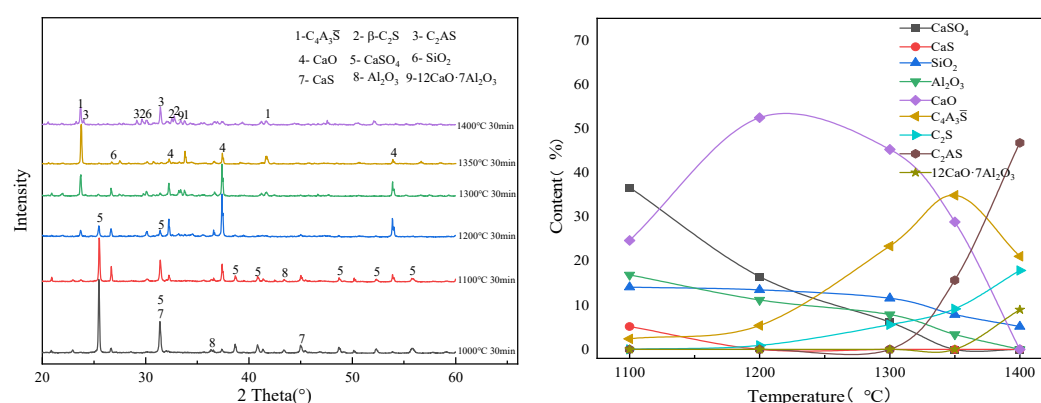


Figure 9. XRD patterns of materials calcined at different temperatures under 2% CO atmosphere, and the trend of each substance's content as a function of temperature.

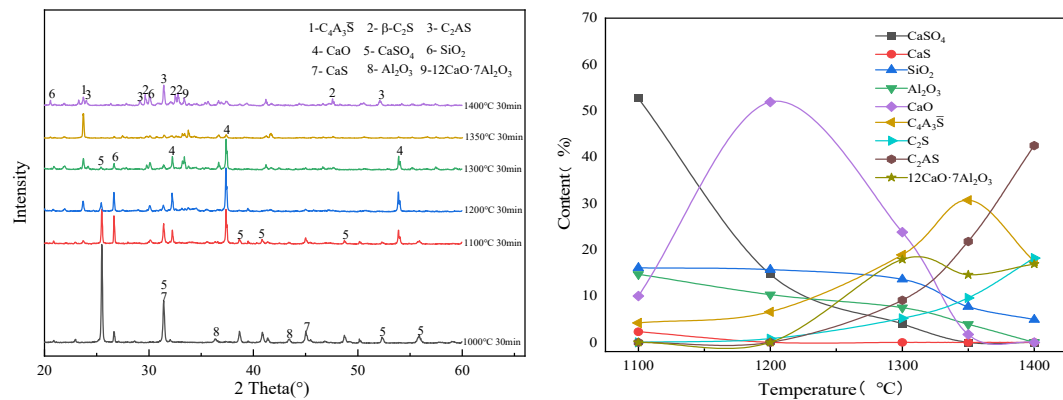


Figure 10. XRD patterns of materials calcined at different temperatures under 3% CO atmosphere, and the trend of each substance's content as a function of temperature.

Under a reducing atmosphere, the content of CaO in the calcined material gradually increases, while the content of $C_4A_3\bar{S}$ decreases with rising CO concentration at temperatures between 1100 °C and 1300 °C. This is due to the fact that under a CO atmosphere, $CaSO_4$ reacts with CO to form CaO, resulting in a significant increase in the CO content of the calcined material, as shown in the reaction equation in Equation (6). When the calcination temperature exceeds 1300 °C, a significant amount of $12CaO \cdot 7Al_2O_3$ is formed in the calcined material.

In summary, $C_4A_3\bar{S}$ begins to form at temperatures above 1100 °C. When the calcination temperature exceeds 1300 °C, C_2AS starts to appear in the calcined material. This occurs because $C_4A_3\bar{S}$ decomposes to produce CaO, which then reacts with SiO_2 and Al_2O_3 to form C_2AS , as shown in Equation (7). Under an oxidizing atmosphere, the main mineral phases in the clinker are $C_4A_3\bar{S}$ and C_2S , with a small amount of the intermediate mineral phase, C_2AS . In contrast, under a reducing atmosphere, the main mineral phases are C_2AS and C_2S , along with a certain amount of $12CaO \cdot 7Al_2O_3$. This is due to the decomposition of $C_4A_3\bar{S}$ to form $12CaO \cdot 7Al_2O_3$ in the reducing atmosphere. The transformation of clinker mineral phases with respect to the calcination temperature under a CO atmosphere is presented in Table 4, from which the generation and transformation temperatures of each clinker mineral phase can be seen.

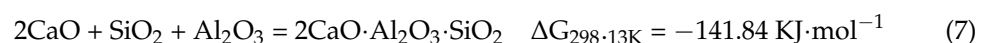


Table 4. The transformation of clinker mineral phases with respect to the calcination temperature under CO atmosphere.

Temperature	Clinker Mineral Phase
1000 °C	$CaSO_4$, CaS, SiO_2 , Al_2O_3
1100 °C	$C_4A_3\bar{S}$, $CaSO_4$, CaS, SiO_2 , Al_2O_3 , CaO
1200 °C	$C_4A_3\bar{S}$, $CaSO_4$, SiO_2 , CaO, C_2S
1300 °C	$C_4A_3\bar{S}$, $CaSO_4$, SiO_2 , CaO, C_2S , $12CaO \cdot 7Al_2O_3$
1350 °C	$C_4A_3\bar{S}$, C_2S , C_2AS , $12CaO \cdot 7Al_2O_3$, CaO
1400 °C	$C_4A_3\bar{S}$, C_2S , C_2AS , $12CaO \cdot 7Al_2O_3$

The infrared spectra of sulphoaluminate cement clinker prepared at different calcination temperatures are illustrated in Figure 11. The absorption band at 411 cm^{-1} is attributed to the bending vibration of (AlO_4) in $C_4A_3\bar{S}$, while the absorption band at 881 cm^{-1} is due to the asymmetric stretching vibration of (AlO_4^{5-}) in $C_4A_3\bar{S}$, where the absorption band at 1102 cm^{-1} is caused by the asymmetric telescoping vibration of (SO_4) . The symmetric

stretching vibration of the Al-O bond occurs in the range of 500–800 cm^{-1} , while the bending vibration of (SO_4) is found in the range of 600–700 cm^{-1} . Consequently, vibrational coupling between (AlO_4) and (SO_4) in this wavenumber interval results in three absorption peaks at 610 cm^{-1} , 641 cm^{-1} , and 691 cm^{-1} , as illustrated in the figure. The absorption band at 520 cm^{-1} is attributed to the bending vibration of (SiO_4), and the absorption band at 1000 cm^{-1} is due to the asymmetric stretching vibration of (SiO_4) [24]. In summary, the characteristic absorption bands of $\text{C}_4\text{A}_3\bar{\text{S}}$ are found at 1102 cm^{-1} , 881 cm^{-1} , 610 cm^{-1} , 641 cm^{-1} , 691 cm^{-1} , and 411 cm^{-1} . The characteristic absorption bands of C_2S are observed at 520 cm^{-1} and 1000 cm^{-1} . When the calcination temperature reaches 1200 °C, the characteristic absorption band of C_2S appears on the spectrum, indicating the formation of C_2S . The intensity of the C_2S absorption band increases progressively with higher calcination temperatures. At the same time, as the calcination temperature increases, the peak intensity of the characteristic absorption band of $\text{C}_4\text{A}_3\bar{\text{S}}$ also gradually strengthens. However, after the calcination temperature exceeds 1300 °C, the peak intensity begins to decrease. This indicates that a moderate increase in temperature promotes the formation of $\text{C}_4\text{A}_3\bar{\text{S}}$, while excessively high temperatures lead to its decomposition. These findings are consistent with the XRD spectra analysis results.

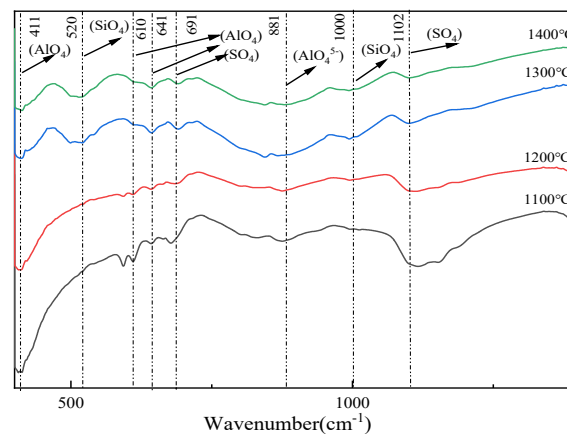


Figure 11. Infrared spectra of sulphoaluminate cement clinker prepared at various calcination temperatures.

The micro-morphological analysis of cement clinker at different calcination temperatures is illustrated in Figure 12. As the calcination temperature increases, the $\text{C}_4\text{A}_3\bar{\text{S}}$ grains gradually aggregate and grow, forming polygonal plate-like structures with well-defined contours and clear grain boundaries, with a grain size of approximately 1–2 microns. At 1300 °C, the $\text{C}_4\text{A}_3\bar{\text{S}}$ grains are generally large and concentrated, whereas at 1400 °C, the $\text{C}_4\text{A}_3\bar{\text{S}}$ grains become more dispersed and smaller in size. These observations align with the changes in the mineral phase of $\text{C}_4\text{A}_3\bar{\text{S}}$ at various calcination temperatures, indicating that excessively high temperatures lead to the decomposition of $\text{C}_4\text{A}_3\bar{\text{S}}$ [9].

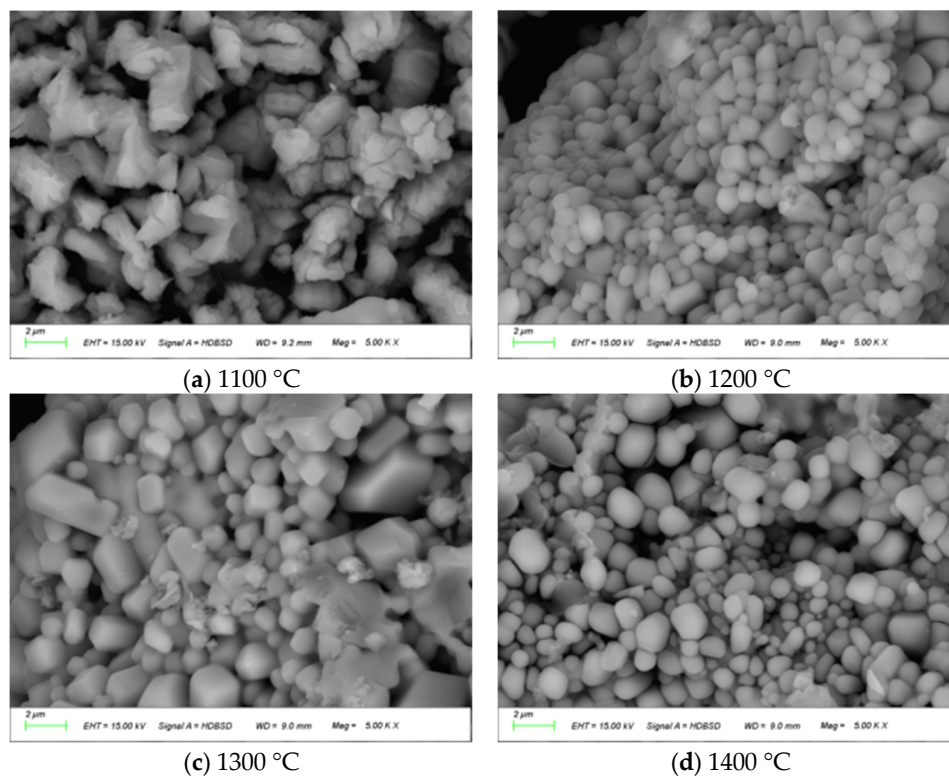


Figure 12. SEM analysis of clinker at various calcination temperatures.

3.2. Effect of Calcination Time on the Evolution of the Main Mineral Phases of Clinker

Figure 13 illustrates the XRD pattern of the material calcined at 1300 °C under a N_2 atmosphere for varying times. The figure indicates that at a constant calcination temperature, the intensity of the diffraction peaks for the clinker mineral phases $C_4A_3\bar{S}$ and C_2S increases with longer calcination times. This suggests that extending the calcination time enhances the formation of these mineral phases in the cement clinker.

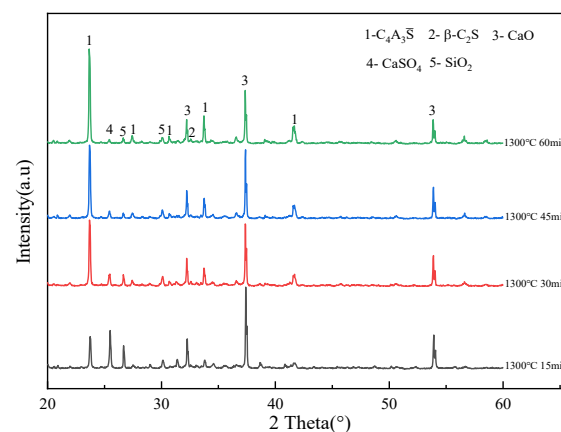


Figure 13. XRD patterns of materials calcined at 1300 °C under N_2 for different durations.

Figure 14 illustrates the XRD patterns of the material calcined at 1300 °C for various durations in 1% O_2 , 2% O_2 , and 3% O_2 atmospheres. The figure reveals that under oxygen-poor conditions, the diffraction peak intensities of the clinker mineral phases $C_4A_3\bar{S}$ and C_2S increase with longer calcination times. In contrast, under oxygen-rich conditions, $CaSO_4$ reacts with CaS to form CaO , leading to a rise in $CaSO_4$ content and a decrease in CaO content. This reduction in available CaO limits the formation of $C_4A_3\bar{S}$, resulting in some $CaSO_4$ remaining in the clinker and not participating in the clinker mineral phase formation.

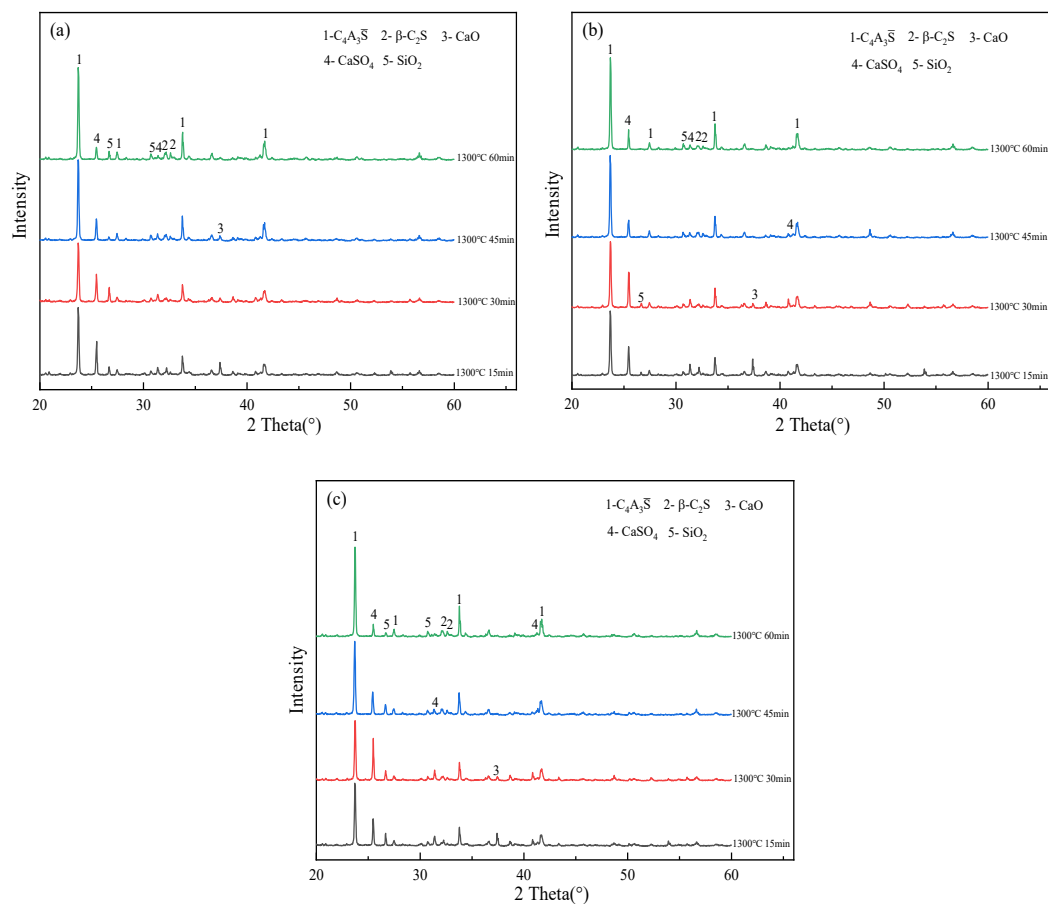


Figure 14. XRD patterns of materials calcined at 1300 °C for different durations: (a) 1%O₂, (b) 2%O₂, and (c) 3%O₂.

Figure 15 illustrates the XRD patterns of materials calcined at 1300 °C for different durations in 1% CO, 2% CO, and 3% CO atmospheres, along with the corresponding trends in the content of each substance with respect to calcination time. Under 2–3% CO atmospheres, the intensity of the diffraction peaks for $C_4A_3\bar{S}$ decreases with increasing calcination time, while significant amounts of $12CaO \cdot 7Al_2O_3$ and CaO appear in the calcined material. At 1300 °C, $CaSO_4$ undergoes decomposition to produce CaO, resulting in a gradual decrease in the intensity of the characteristic diffraction peaks for $CaSO_4$, and an increase in the content of CaO in the material calcined at this temperature. The results indicate that under a reducing atmosphere, the decomposition of $CaSO_4$ inhibits the formation of the $C_4A_3\bar{S}$ phase, leading to a transformation of the main mineral phases in the clinker into C_2AS and $12CaO \cdot 7Al_2O_3$.

In summary, the diffraction peak intensities of the clinker mineral phases $C_4A_3\bar{S}$ and C_2S in the calcined material increase with extended calcination time under both N₂ and O₂ atmospheres. This indicates that prolonging the calcination time is beneficial for the formation of cement clinker mineral phases. In contrast, under a CO atmosphere, the diffraction peak intensity of the clinker mineral phase, $C_4A_3\bar{S}$, decreases, while the quantities of $12CaO \cdot 7Al_2O_3$ and CaO increase significantly in the calcined material. This shift indicates that under reducing conditions, the primary compositions of the calcined material become C_2AS , $12CaO \cdot 7Al_2O_3$, and CaO, demonstrating that $C_4A_3\bar{S}$ is prone to decomposition in a reducing atmosphere.

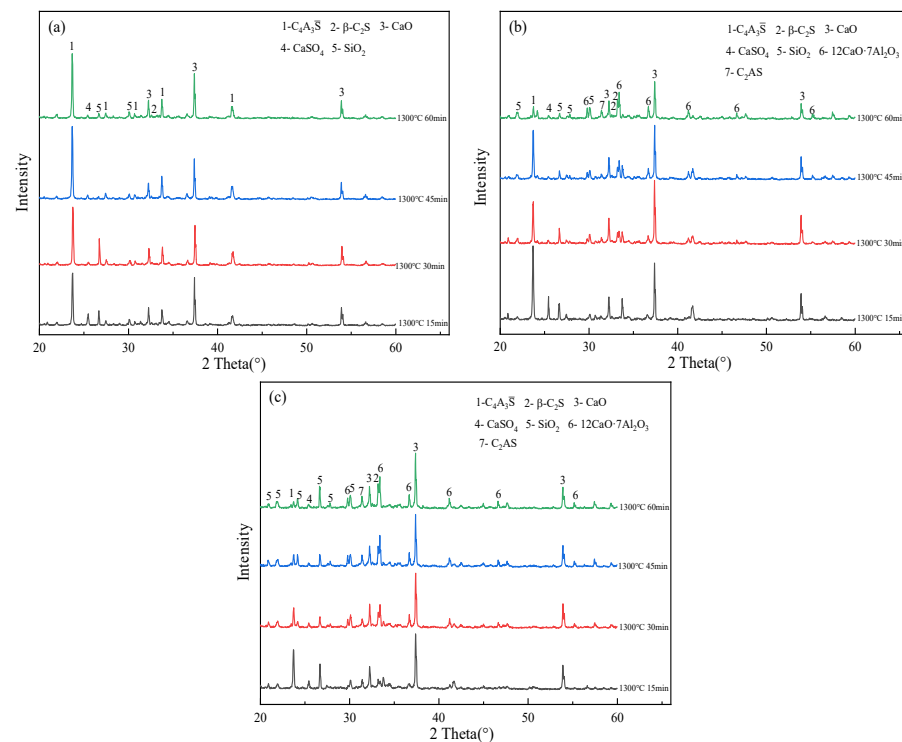
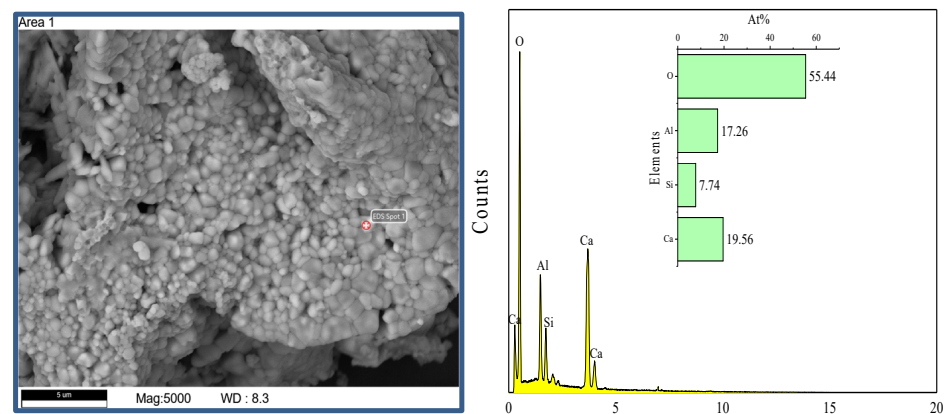
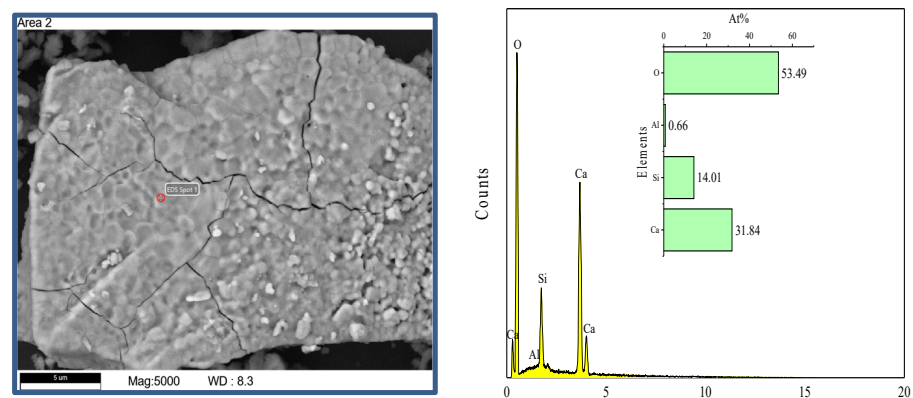
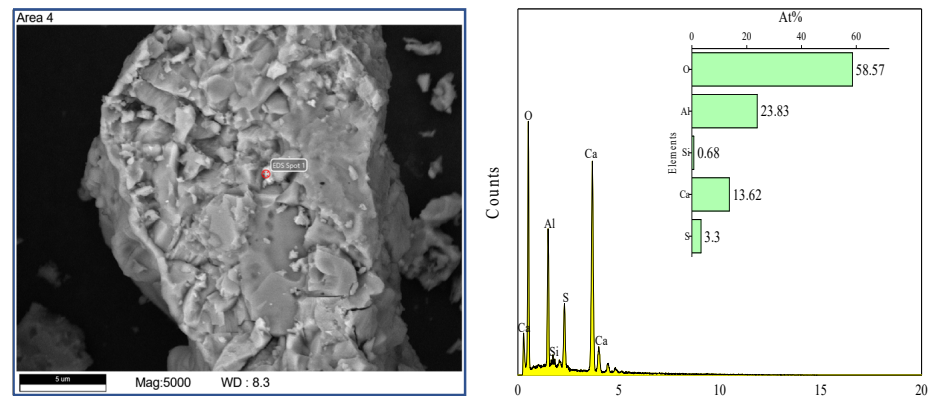


Figure 15. XRD patterns of materials calcined at 1300 °C for different durations: (a) 1%CO, (b) 2%CO, and (c) 3%CO.

The mineral phases of sulphoaluminate cement clinker were qualitatively analyzed through backscattered scanning electron microscopy to examine the micro-morphology of the samples. Energy spectroscopy in a point-scan format was employed to analyze the clinker and verify the elements present in the three different mineral phases. The elemental compositions at each point of the clinker are summarized in Table 5. The energy spectrum analyses for the three different mineral phases are illustrated in Figure 16. Spectrum (a) shows a Ca:Al:Si:O ratio of 2.53:2.22:1:7.16, which is similar to the ratio of the number of atoms in C_2AS (molecular formula $Ca_2Al_2SiO_7$). Spectrum (b) shows a Ca:Si:O ratio of 2.27:1:3.82, which resembles the atomic ratio in C_2S (molecular formula Ca_2SiO_4). Spectrum (c) shows a Ca:Al:O:S ratio of 4.13:7.22:17.75:1, which aligns with the atomic ratio in $C_4A_3\bar{S}$ (molecular formula $Ca_4Al_6(SO_4)O_{12}$).

Table 5. Atomic proportions of mineral phase elements in clinker (%).

	O	Al	Si	Ca	S
a	55.44	17.26	7.74	19.56	/
b	53.49	0.66	14.01	31.84	/
c	58.57	23.83	0.68	13.62	3.3

(a) EDS energy spectrum analysis—C₂AS(b) EDS energy spectrum analysis—C₂S(c) EDS energy spectrum analysis—C₄A₃S̄**Figure 16.** EDS spectrum analysis of sulphotoaluminate cement clinker.

3.3. Influence of O₂ Content in the Oxidizing Atmosphere on the Evolution of Main Mineral Phases in Clinker

Figure 17 illustrates the XRD patterns of the calcined materials obtained with different O₂ contents with a calcination time of 30 min and at calcination temperatures ranging from 1000 °C to 1400 °C. The figure shows that the intensity of the characteristic diffraction peaks of C₄A₃S̄ initially increases and then decreases with rising oxygen content under an oxidizing atmosphere. Moreover, the reaction between CaS and O₂ under an oxidizing atmosphere generates additional CaSO₄. This shifts the reaction equilibrium of $3\text{CaO} + \text{CaSO}_4 + 3\text{Al}_2\text{O}_3 = 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ positively, leading to increased formation of C₄A₃S̄. However, as the reaction progresses, the decreasing content of CaO in the calcined material shifts the equilibrium negatively, causing the content of C₄A₃S̄ to gradually

decrease. The decomposition of $C_4A_3\bar{S}$ into C_2AS occurs at excessively high calcination temperatures, particularly after 1350 °C. At 1350 °C with 1% O_2 , the intensity of the characteristic diffraction peaks of C_2AS is the lowest, indicating minimal formation of C_2AS under these conditions. The reason for this is that the amounts of $CaSO_4$ and CaO in the calcined material significantly influence the formation of the clinker mineral phases $C_4A_3\bar{S}$ and C_2AS . Insufficient $CaSO_4$ or CaO content in the calcined material leads to inadequate formation of $C_4A_3\bar{S}$ during the reaction. Consequently, the transitional mineral phase C_2AS cannot effectively react with CaO to form $C_4A_3\bar{S}$, resulting in its persistence in the clinker and a reduction in clinker quality.

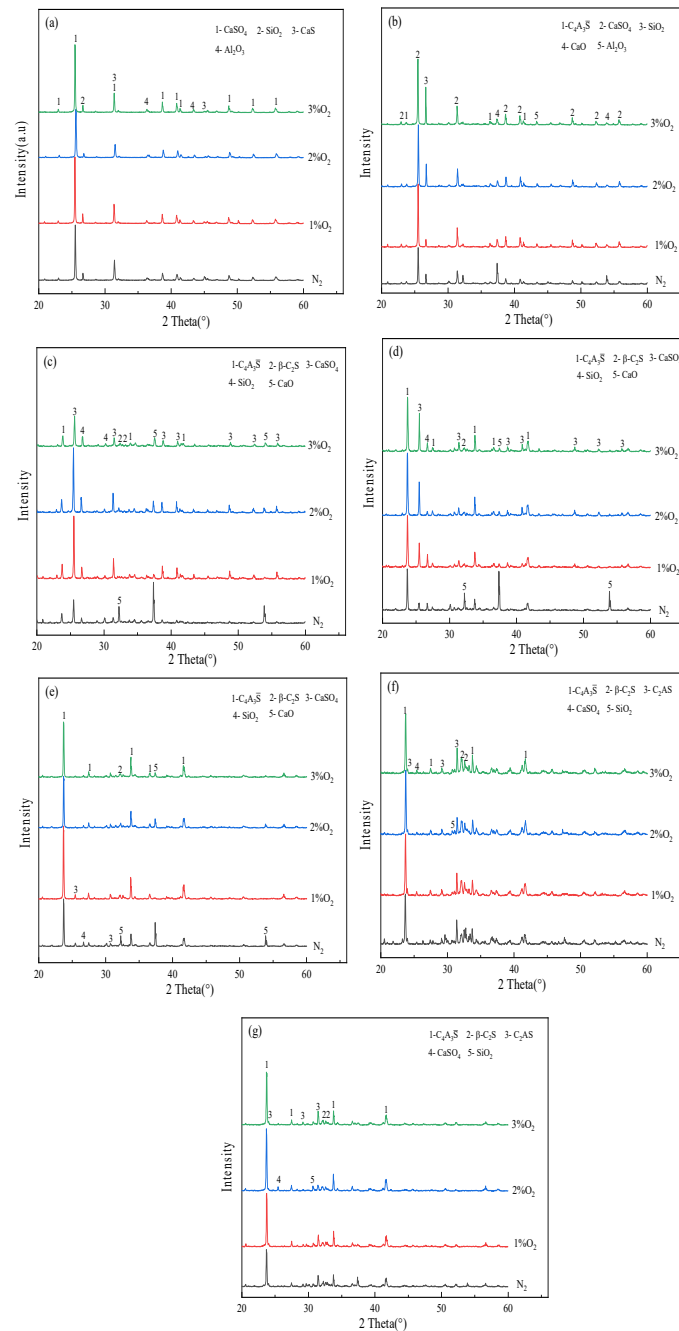


Figure 17. XRD comparison of calcined materials with different O_2 contents: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1350 °C, (f) 1380 °C, and (g) 1400 °C.

3.4. Effect of CO Content in a Reducing Atmosphere on the Evolution of the Main Mineral Phases in Clinker

Figure 18 compares the XRD patterns of the calcined materials with varying CO contents, obtained with a calcination time of 30 min and at temperatures of 1000 °C–1400 °C. The characteristic diffraction peaks of $C_4A_3\bar{S}$ decrease as the CO content increases in the reducing atmosphere. This trend is due to the inhibiting effect of a reducing atmosphere on the reaction between CaO and $CaSO_4$ to form $C_4A_3\bar{S}$. Additionally, C_2AS appears in the material calcined at 1300 °C under a 3% CO atmosphere, indicating that a reducing atmosphere favors the formation of the inert mineral phase, C_2AS . After the calcination temperature exceeds 1300 °C, the relative intensity of the characteristic diffraction peaks of $CaSO_4$ in the clinker significantly decreases, while the intensity of the diffraction peaks of CaO notably increases, because $CaSO_4$ reacts with CO to form CaO, SO_2 , and CO_2 . Furthermore, when the calcination temperature reaches 1300 °C, $CaSO_4$ decomposes to form CaO. This decomposition reaction inhibits the formation of the clinker mineral phase, $C_4A_3\bar{S}$. At a calcination temperature of 1400 °C, as the CO content increases, the intensity of the characteristic diffraction peaks of C_2AS and $12CaO \cdot 7Al_2O_3$ in the calcined material gradually increases, while the intensity of the characteristic diffraction peaks of $C_4A_3\bar{S}$ decreases. Consequently, under a higher reducing atmosphere, the main mineral phases in the clinker are transformed into C_2AS and $12CaO \cdot 7Al_2O_3$.

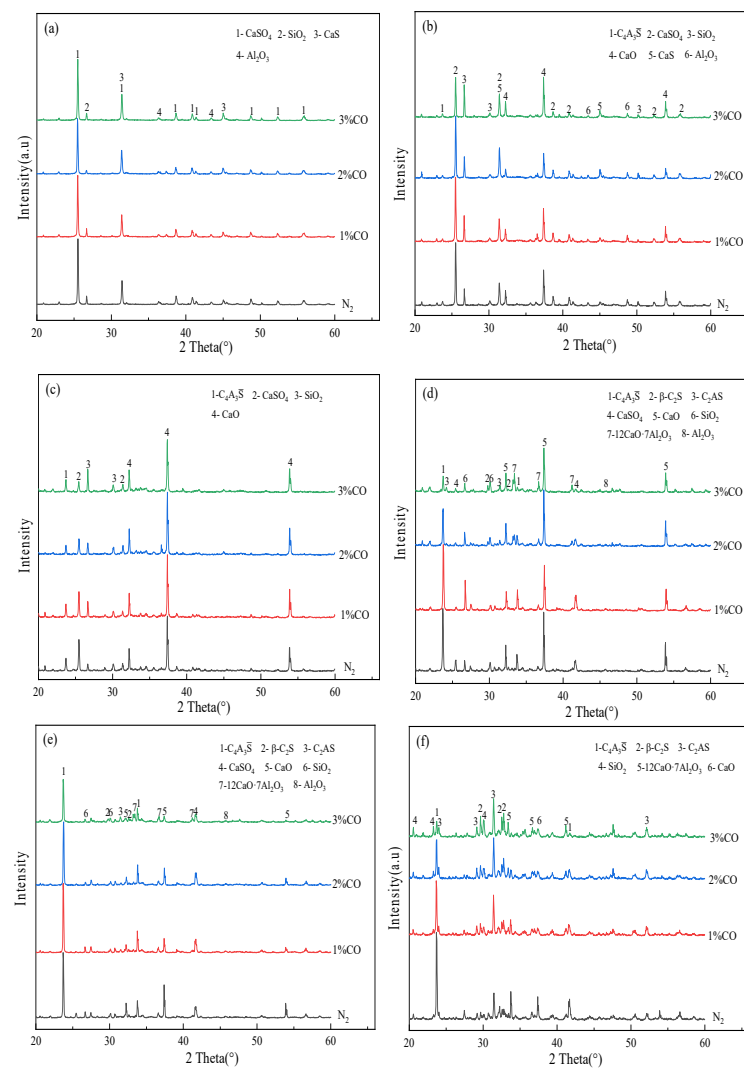


Figure 18. XRD comparison of calcined materials with different CO contents: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1350 °C, and (f) 1400 °C.

In summary, after the calcination temperature exceeds 1300 °C under a reducing atmosphere, a significant amount of C_2AS and $12CaO \cdot 7Al_2O_3$ is formed in the clinker. This indicates that the formation of the clinker mineral phase, $C_4A_3\bar{S}$, is inhibited by the decomposition of $CaSO_4$ in the reducing atmosphere, leading to a transformation of the main mineral phases in the clinker to C_2AS and $12CaO \cdot 7Al_2O_3$.

4. Conclusions

This paper investigated the mechanism of mineral phase transformation in clinker during the cogeneration of sulphoaluminate cement clinker through the gas-phase sulphur reduction of phosphogypsum for acid production. The effects of different calcination regimes on the generation of mineral phases in cement clinker were designed and studied. The following conclusions can be drawn:

The formation of the main mineral phase, $C_4A_3\bar{S}$, in clinker begins at 1100 °C. An increase in the calcination temperature or an extension of the calcination time enhances the formation of $C_4A_3\bar{S}$. However, after the temperature reaches 1350 °C, C_2AS begins to appear in the clinker, indicating that $C_4A_3\bar{S}$ decomposes at higher temperatures to form C_2AS .

Under N_2 and oxidizing atmospheres, the primary mineral phase in clinker is $C_4A_3\bar{S}$, with some amounts of C_2S and C_2AS . The content of both $C_4A_3\bar{S}$ and C_2S in the clinker increases with the extension of the calcination time.

In a CO atmosphere, the main mineral phases in clinker are C_2AS and $12CaO \cdot 7Al_2O_3$. The decomposition of $CaSO_4$ inhibits the formation of the clinker mineral phase, $C_4A_3\bar{S}$, resulting in a significant increase in C_2AS in the calcined material once the calcination temperature exceeds 1300 °C, and $12CaO \cdot 7Al_2O_3$ begins to form. As the calcination time is extended, the content of $C_4A_3\bar{S}$ in the clinker decreases, while the content of C_2AS and $12CaO \cdot 7Al_2O_3$ increases.

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