

Article

Effects of $C\$H_2$ and CH on Strength and Hydration of Calcium Sulphoaluminate Cement Prepared from Phosphogypsum

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Abstract: Using phosphogypsum (PG) as a raw material to prepare calcium sulphoaluminate cement (CAS) is an effective way of treating phosphogypsum. In order to meet the different application requirements of CSA cement and promote the application of CAS cement, it is necessary to add mineral admixtures to adjust the performance of cement. This paper incorporated two minerals, gypsum dihydrate ($C\$H_2$) and calcium hydroxide (CH), into cement clinker prepared from phosphogypsum. The compressive strength and hydration process of the mixtures with different blending levels were investigated around the $C_4A_3\$\text{-}C\H_2 system (SC) and the $C_4A_3\$\text{-}C\$H_2\text{-}CH$ system (SCC). The optimum dosing level was determined on the basis of the strength and hydration properties. In the SC system, adding $C\$H_2$ promoted the hydration of $C_4A_3\$$. The compressive strength of the cement was highest at a $C\$H_2/C_4A_3\%$ molar ratio of 1.5, with a 7-day compressive strength of 56.5 MPa. Aft was mostly needle-rod and columnar and was tightly cemented to the gel phase, improving the denseness of the matrix. When the molar ratio was 2, the strength of the cement was inverted, and the shape of the Aft changed from needle and rod to columnar, the size of the grains increased, and it could not be filled with the AH_3 phase in an excellent staggered manner. At the same time, $C\$H_2$ was not fully reacted, increasing matrix porosity and inversion of strength. In the SCC system, adding CH reduced the cement's compressive strength, and the compressive strength reduction increased with the increase in admixture. According to the experimental results, CH inhibited the formation of Aft, resulting in the appearance of new hydration products, AFm. As the amount of CH increased, the amount of hydration products, AFm, increased, while the amount of Aft and AH_3 decreased. However, adding CH raised the paste's pH and later facilitated the development of strength. The optimum admixture of $CH/C_4A_3\%$ was 0.5 mol.

Keywords: phosphogypsum; calcium sulphoaluminate aluminate cement; gypsum; calcium hydroxide; strength; hydration properties



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1. Introduction

Phosphogypsum (PG), as an industrial waste product emitted from the production of phosphoric acid, contains about 4–5 tonnes of phosphogypsum per tonne of phosphoric acid produced [1,2]. The main component of phosphogypsum is gypsum dihydrate, with a content of up to 85% or more, making it a gypsum resource that cannot be ignored [3,4]. The phosphate industry continues to develop, and the corresponding phosphogypsum emissions are increasing. According to statistics, about 280 million tonnes of phosphogypsum are emitted worldwide in one year, with only about 10% being used effectively [5,6]. Phosphogypsum contains small amounts of under-reacted sulphuric acid, phosphoric acid, phosphide, fluoride, and other impurities, resulting in its low utilisation rate [7–9]. Large amounts of untreated phosphogypsum are piled on land, polluting the environment and restricting economic development [10–12]. The way in which to deal with phosphogypsum is a current problem to be solved. The application of phosphogypsum to construction

materials, with high consumption and low side effects on the environment, has the best prospects for utilisation and is thus the main focus of researchers [13–15].

Phosphogypsum is used to prepare gypsum cementitious materials, and impurities can lead to longer setting times, reduced material density and strength, and poor durability [16]. When used as a silicate cement retarder, phosphogypsum contains phosphorus, fluorine, and other harmful impurities and a lower pH [17], so the application performance is negatively affected; thus, the phosphogypsum must be pretreated. Pretreatment increases not only the cost of the process and the difficulty of use but also causes the treatment to not be good, thus making the phosphogypsum utilisation rate very low [18]. Scholars have attempted to prepare CSA cement from phosphogypsum to improve the utilisation of phosphogypsum [19,20]. Studies have shown that P_2O_5 and F- impurities in phosphogypsum promote the formation of clinker minerals and lower firing temperatures [21,22]. However, pollutants in the clinker lead to increased setting times and reduced pH and strength, which are not conducive to large-scale use of the cement [1,23]. Mineral admixtures such as gypsum and lime are usually added to adjust cement properties to meet the requirements of cement used in different environments [24]. During the hydration of $C_4A_3\$$, both gypsum and pH have an important influence on the hydration reaction [25]. Winnfield et al. found that anhydrous gypsum slowed the initial rate of $C_4A_3\$$ hydration compared to gypsum dihydrate [26]. Hargis et al. studied the hydration system of $C_4A_3\$-C\H_2-CH . They found that the incorporation of CH retarded the formation of AFt crystals and was associated with ye'elimite surface collocation [27]. However, for CAS cement prepared from phosphogypsum, few studies have been reported on the influence of the mineral admixtures gypsum and lime on their properties and hydration processes. Therefore, it is essential to study the effects of different doping amounts of gypsum and lime on the strength, hydration products, pH, and hydration process of PG-CAS cement for the promotion and application of cement and the resourcefulness of phosphogypsum.

In this paper, CAS cement clinker was prepared using PG as raw material, and the clinker's mineral composition was determined in order to meet the requirements. Then $C\$H_2$ and CH were added in different ratios to construct the $C_4A_3\$-C\H_2 system and the $C_4A_3\$-C\H_2-CH system. The compressive strength, pH, and hydration process of the cement of the SC and SCC systems were investigated. XRD and TG-DTG were used to analyse the changes in hydration products. SEM and MIP observed microscopic morphological changes to verify the development of macroscopic properties. It was hoped that the effect of mixing the three minerals $C_4A_3\$$, $C\$H_2$, and CH in different mix ratios on the strength and hydration process of the cement would be obtained. The work contributes to the promotion and application of PG-CAS cement-based materials.

2. Experimental Program

2.1. Materials

The raw materials used in this paper were bauxite, phosphogypsum, and limestone from the Guizhou Urnford Group. All raw materials were ground by a planetary ball mill and passed through an 80 μm sieve with a residue rate of less than 5%. The chemical composition of the raw materials is listed in Table 1. The target phase combination for the calcium sulphoaluminate cement was 70% $C_4A_3\$$, 16% C_2S , 8% C_4AF , and 6% $C\$$. On the basis of the target phase combination and the chemical composition of the raw materials shown in Table 1, the formulation of the CAS cement raw material was determined, as shown in Table 2. The ground raw materials were accurately weighed and homogenised according to the ratios in Table 2. The raw material mixture was mixed with 10 wt% water and made into $\Phi 5 \times 1.5$ cm round cakes under 8 MPa pressure. The clinker was dried in an oven at 40 °C and then placed in a high-temperature furnace for firing at a heating rate of 10 °C/min, calcination temperature of 1250 °C, and a holding time of 1 h [28]. After calcination, the clinker was removed for rapid cooling, and after cooling, the clinker was ground with a planetary ball mill for 5 min and then finely ground with an agate mortar and passed through an 80 μm sieve. As shown in Figure 1, the XRD curves had distinct

peaks characteristic of the clinker minerals, mainly C_4A_3S , C_2S , C_2AS , and $C\$$. The Rietveld method was used to quantify the cement clinker minerals and determine the content of each phase in the clinker. The quantification results are shown in Table 3. The XRD profiles had good profile fitting ($R_{wp} < 15\%$) [29–31], and the quantification results were reliable. The microscopic morphology of the prepared CAS clinker is shown in Figure 2. The clinker minerals were mostly C_4A_3S , in the form of hexagonal plates or round grains, 1–2 μm in size, with a smooth surface and tightly arranged. The prepared calcium sulphoaluminate cement clinker was mixed and ground with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ in the proportions shown in Table 4. Figure 3 shows the flow chart for this experiment.

Table 1. Chemical compositions of the materials (wt%).

Materials	SO_3	CaO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	P_2O_5	F
PG	53.04	41.48	3.32	0.24	0.40	0.07	-	0.81	0.64
Limestone	0.24	89.68	3.75	0.94	0.77	-	4.62	-	-
Bauxite	6.25	0.47	9.82	72.72	5.19	5.33	0.22	-	-

Table 2. Proportioning of the cement raw meal (wt%).

Sample	Limestone	Phosphogypsum	Bauxite
S	39.44	22.67	37.89

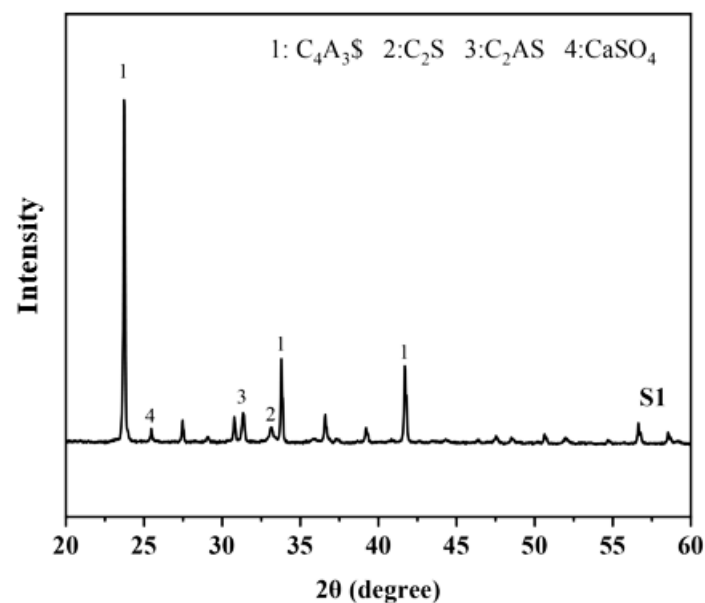


Figure 1. XRD pattern of the clinkers calcined at 1250 °C for 60 min.

Table 3. Contents of cement clinker minerals (wt%).

Sample	Phase Content (wt%)					R_{wp} (%)
	C_4A_3S	C_2S	C_4AF	$C\$$	C_2AS	
S	73.00	13.54	5.42	5.26	2.78	12.76

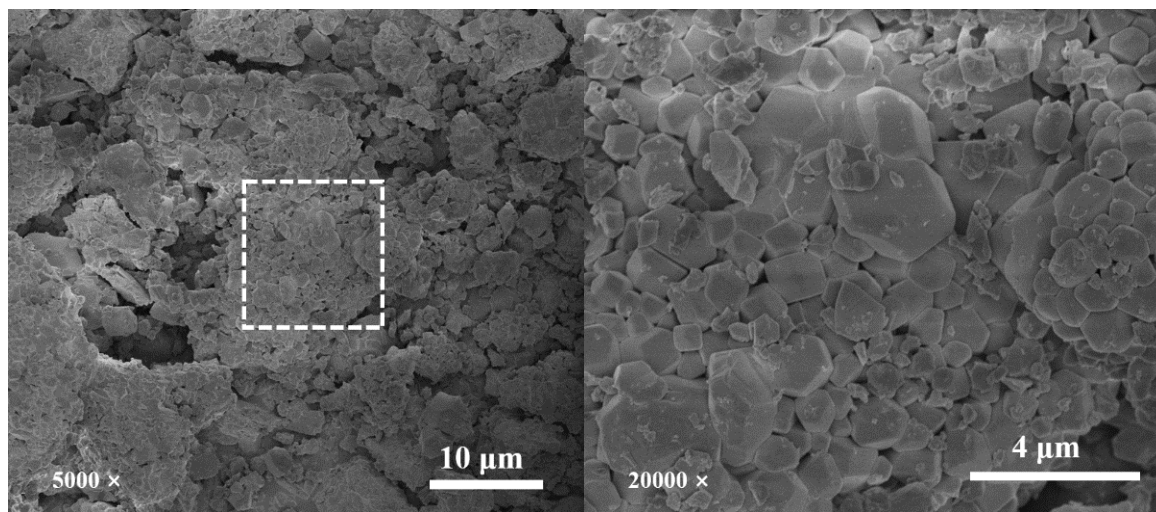


Figure 2. SEM-SE morphology of cement clinkers.

Table 4. Mineralogical phase in samples SC1–SC3 and SCC1–SCC3.

Sample	The Molar Ratio of C_2S to C_4A_3	The Molar Ratio of CH to C_4A_3	wt%		
			Clinker/ C_4A_3	C_2S	CH
SC1	1.0	0	82.10/59.93	17.90	0
SC2	1.5	0	76.90/56.14	23.10	0
SC3	2.0	0	70.90/51.76	29.10	0
SCC1	1.5	0.25	103.97/75.90	22.70	1.40
SCC2	1.5	0.50	102.6/74.90	22.48	2.62
SCC3	1.5	0.75	101.34/73.98	22.19	3.83

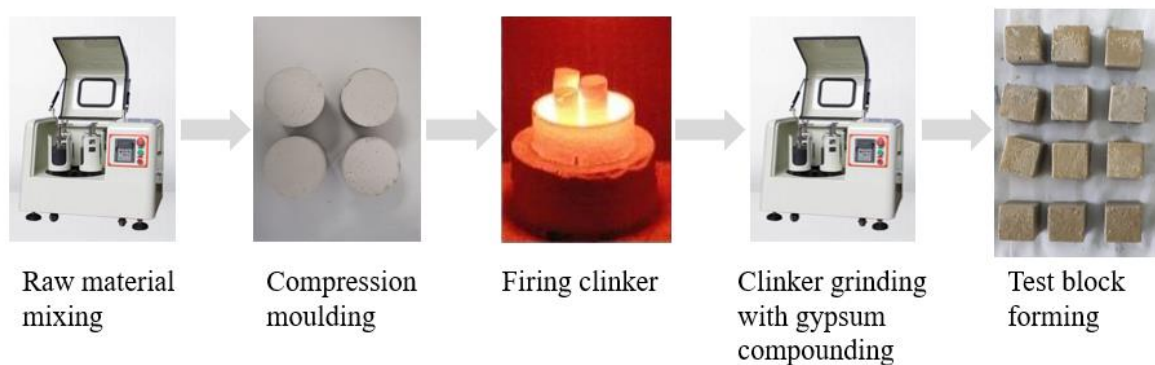


Figure 3. Experimental flowchart.

2.2. Test Methods

The samples were prepared using the water-to-cement ratio of 0.5 and a $20 \times 20 \times 20$ mm mould. The moulds were placed in a standard curing room at a temperature of $(20 \pm 1)^\circ\text{C}$ and $(95 \pm 1)\%$ humidity for curing and moulding. The moulds were removed after curing age for 1 day, and the samples were placed in the standard curing room. The cube samples were cured in the standard curing room, and the compressive strength of the cement paste was determined at 1, 3, 7, and 28 days. The test blocks were tested for compressive strength using six cube samples for the compression test, and the average value was the final compressive strength.

At the end of the compression test, the hydrated samples were placed in acetone for 24 h to terminate the hydration, after which the blocks were dried in an oven at 40°C for

24 h. After drying, the samples were ground in a mortar and passed through an 80 μm square-hole sieve. The samples were analysed by XRD (Bruker D8 Advance). The test range was 5–80° (2 θ) with a single step scan time of 0.5 s at a step size of 0.02°. The sample phase was detected using EVA software and quantified using TOPAS 4.2 software.

The weight loss of the different samples was tested using an integrated calorimetric analyser (Mettler-Toledo TGA/DSC1, Switzerland) in a dry nitrogen environment at 50 mL/min. The samples were placed in an alumina crucible at a temperature of 50–1000 °C with a heating rate of 10 °C/min. The DTG curve was obtained by solving the TG curve in the first order, which reflects the decomposition peaks corresponding to the decomposition of the different phases. The pore solution was prepared by mixing the sample with deionised water in a 10:1 liquid to solid ratio, then stirred for 2 h with a magnetic mixer and filtered.

The pore size distribution and porosity of the sample in the middle of the 2 g block (3–5 mm) were tested by an automatic pore structure analyser (AutoPore IV 9500, USA). The morphology and particle size of the hydration products were analysed using a scanning electron microscope (FEI Quanta 450, USA). Gold spray coating of samples was at 30 Pa, 15 mA.

3. Results and Discussion

3.1. Compressive Strength

Figure 4 shows the compressive strength of six groups of samples at different curing times. The compressive strengths of SC1 specimens at 1, 3, 7, and 28 days were 34.8, 41.9, 45.4, and 47.8 MPa, respectively. With increasing C SH_2 admixture, the strength of SC2 increased by approximately 14.1, 18.85, 24.23, and 22.6% compared to SC1 specimens. The strength of SC3 specimens at different curing times were 40.9, 52.4, 52.1, and 49.7 MPa, increasing and then decreasing with increasing hydration time. The addition of C SH_2 has a beneficial effect on the compressive strength of the cement. However, the excessive amount of C SH_2 causes a reduction in the strength of the specimens at a later stage, which is related to the micro-expansion of the cement specimens at the later stage of hydration [32,33]. The compressive strengths of specimens in the SCC1 to SCC3 groups were reduced in the early stages of hydration compared to the SC2 specimens. The reduction in compressive strength increased with increasing amounts of CH. The incorporation of CH reduced the early strength of the cement, which may have been related to the acidity and alkalinity in the environment. As the reaction continued, the strength of SCC2 specimens developed the fastest; by 28 days of age, the compressive strength of SCC2 specimens was close to that of SC2, indicating that adding CH reduced the cement's compressive strength. Still, the appropriate amount of CH benefited the development of the later strength of the paste.

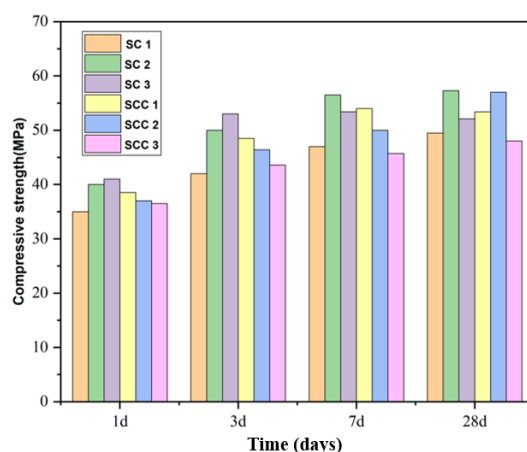


Figure 4. Compressive strength of samples SC1–SC3 and SCC1–SCC3 at different curing times.

3.2. pH Measurement

Figure 5 shows the pH variation at different curing times for samples from the SC2 and SCC1–SCC3 groups. Usually, the pH of calcium sulphoaluminate cement is roughly around 11 to 12; as the raw material, PG has a pH of about 5.8, resulting in a low pH of the prepared cement clinker. The pH values of the four groups of samples were 10.13, 10.32, 10.43, and 10.58. The pH values of the SCC1–SCC3 group increased due to the addition of CH. It can be found that as the hydration reaction proceeded, the pH values of all four groups of samples increased in the early stage of hydration, which may have been due to the large amount of OH^- released by the hydration of clinker minerals and a large amount of water required for AFt generation, increasing solution concentration. As the hydration reaction proceeded, the pH stabilised between the alkali consumption in the solution in equilibrium. Adding CH increased the concentration of Ca^{2+} and OH^- ions in the solution, inhibiting the clinker minerals hydrolysis, resulting in the slow production of AFt in the early stages of hydration, which had a negative impact on the strength development of the specimens. pH analysis results were in good agreement with the compressive strength analysis results.

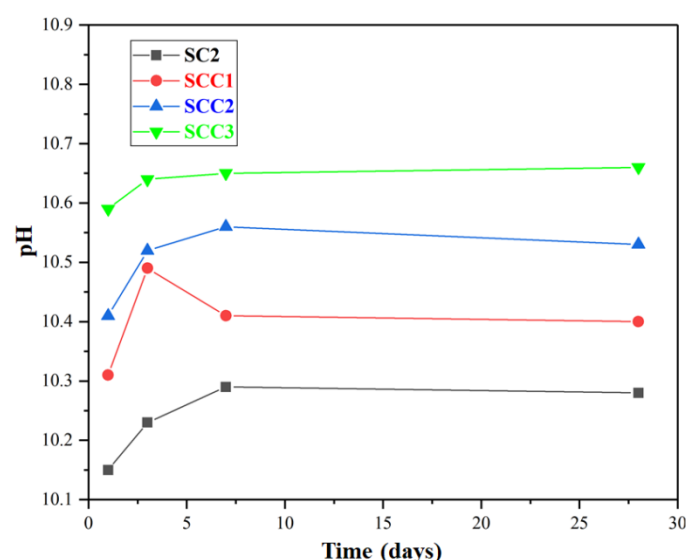
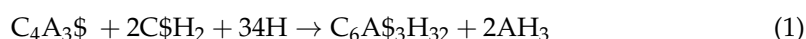


Figure 5. pH value of liquid for cement.

3.3. X-ray Diffraction Analysis

Figure 6 shows the XRD profiles of the six groups of cement samples at 3 days of age. Clear characteristic peaks can be seen in Figure 6, where the main crystalline phases were AFt, AFm, $\text{C}\$\text{H}_2$, and $\text{C}_4\text{A}_3\$\$, and no characteristic peaks of CH were detected, indicating a complete reaction of CH. In the SC1 to SC3 samples, the diffraction peaks of AFt gradually increased with the increase in $\text{C}\$\text{H}_2$ content, indicating that the degree of crystallisation of AFt increased due to the rise of $\text{C}\$\text{H}_2$. Furthermore, in the XRD patterns of the SC1 to SC3 samples, there was no diffraction peak of AFm, which showed that the main hydration reaction of the cement at this time was the typical reaction of $\text{C}_4\text{A}_3\$\$, $\text{C}\$\text{H}_2$, and water to produce AFt and AH_3 ; Equation (1) [29] is shown as follows:



In the samples from SCC1 to SCC3, the content of $\text{C}\$\text{H}_2$ remained unchanged, and with the increase in CH doping, the AFm diffraction peak was gradually apparent. The diffraction peak of $\text{C}_4\text{A}_3\$\$ gradually decreased. It means that the doping of CH made the generation of AFt limited and played an inhibiting role, while there was AFm generation. The following Equation (2) [27] will occur in the system:

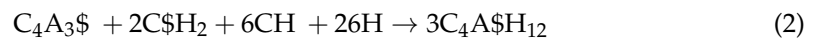


Figure 7 depicts the content of the material phase at the age of 3 days of hydration for the different samples. In the SC1 to SC3 samples, the AFt content of the hydration products increased as the C\$H₂ content gradually increased. However, there was still a tiny amount of C₄A₃\$ remaining, indicating that the hydration was not yet complete. In the SCC1 to SCC3 samples, the more CH was incorporated, the lower the AFt content, and the AFm content of the hydration products increased significantly. The C\$H₂ was able to promote the hydration of C₄A₃\$, causing a large amount of AFt to form in the early stage of hydration. C\$H₂ was able to promote the hydration of C₄A₃\$, resulting in a large amount of AFt formation in the early stage of hydration. The results of the XRD analysis verified the development of the sample strength.

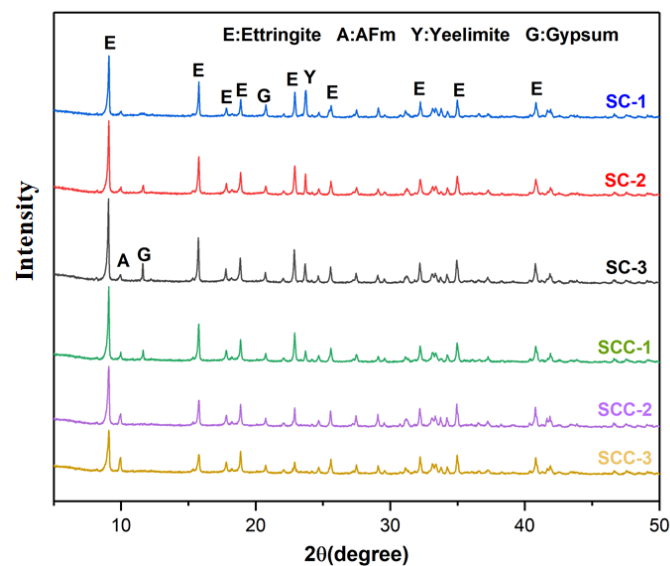


Figure 6. XRD curves of samples SC1-SC3 and SCC1-SCC3 at 3 days of age.

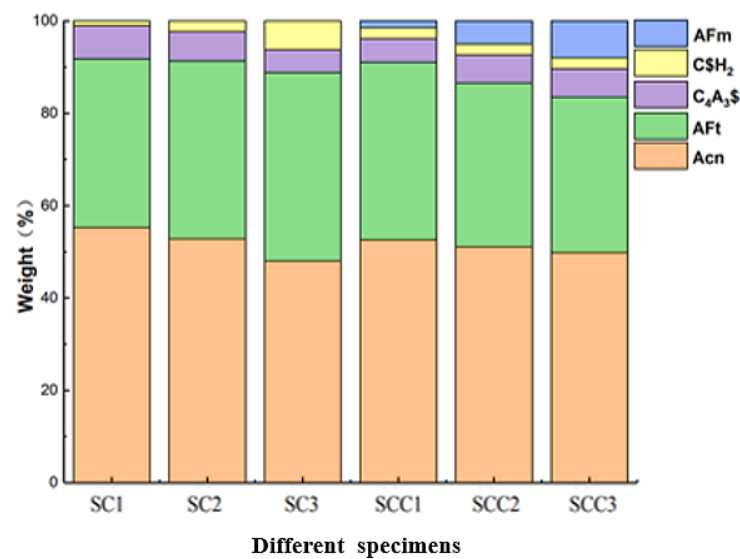


Figure 7. Percentage mass content of samples SC1-SC3 and SCC1-SCC3 at 3 days of age.

3.4. Thermogravimetric Analysis

Figures 8 and 9 show the DTG curves for the hydration products of the SC1 to SC3 and SCC1 to SCC3 samples, respectively. Figure 8 shows three distinct weight loss peaks in the DTG curves. Aft was dehydrated and decomposed in the temperature range of 100–150 °C, C SH_2 was dehydrated and decomposed at around 150 °C, and AH $_3$ was dehydrated and decomposed in the temperature range of 250–275 °C [34–36]. With the increase in C SH_2 content, the mass loss of Aft tended to increase, indicating that the hydration reaction produced more and more Aft, verifying that C SH_2 can promote the hydration reaction and form Aft.

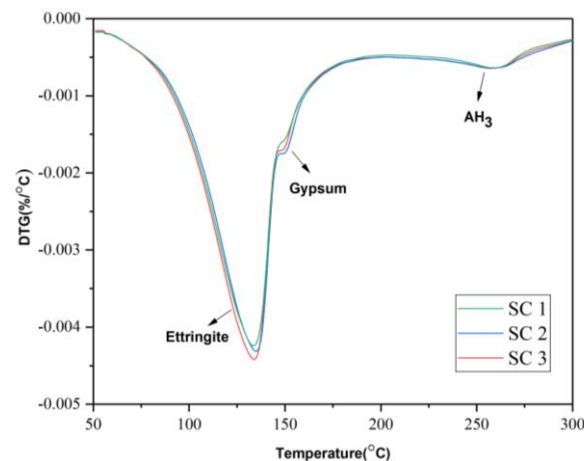


Figure 8. DTG curves of samples SC1-SC3 at 3 days of age.

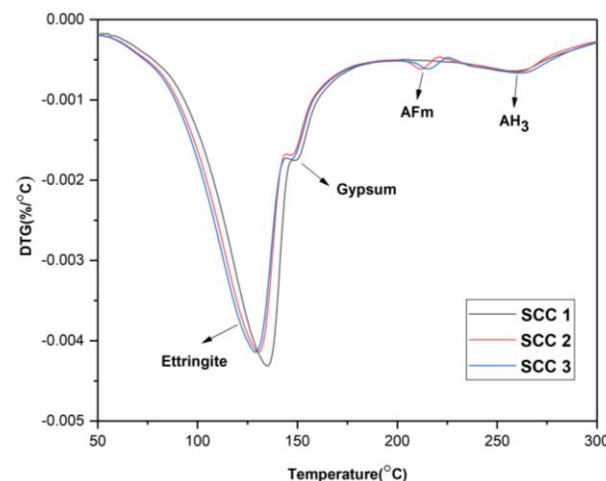


Figure 9. DTG curves of samples SCC1-SCC3 at 3 days of age.

Figure 9 shows the DTG curves of the samples after adding CH. In addition to the weight loss peaks of Aft, C SH_2 , and AH $_3$, a weight loss peak of Afm dehydration decomposition also appeared at around 220 °C. Moreover, the mass loss of Aft decreased, and the mass loss of Afm increased with CH content, indicating that adding CH inhibited the formation of the hydration product Aft and promoted the formation of Afm simultaneously.

3.5. Microstructural Analysis

Figure 10 shows SEM photographs of samples SC1 to SC3 hydrated for 3 days. The Aft and AH $_3$ can be seen clearly in Figure 10; the Aft crystals were interspersed in a pin-rod or columnar shape, forming a spatial network skeleton. The gel phase appeared to be fibrous, interlacing and filling the pores of the Aft crystals and gluing them to each other, hence its dense nature. This interlaced and densely filled structure can improve the

mechanical properties of the cement [37,38]. The AFt in the SC3 sample was relatively large in particle size compared to the other two groups and was not well interleaved and filled with the AH_3 phase. Moreover, the excess C_3H_2 reaction left larger pores, which affected the structure of the cement samples and thus reduced the compressive strength of the cementite. Microscopic morphological observations verified the development of macroscopic properties.

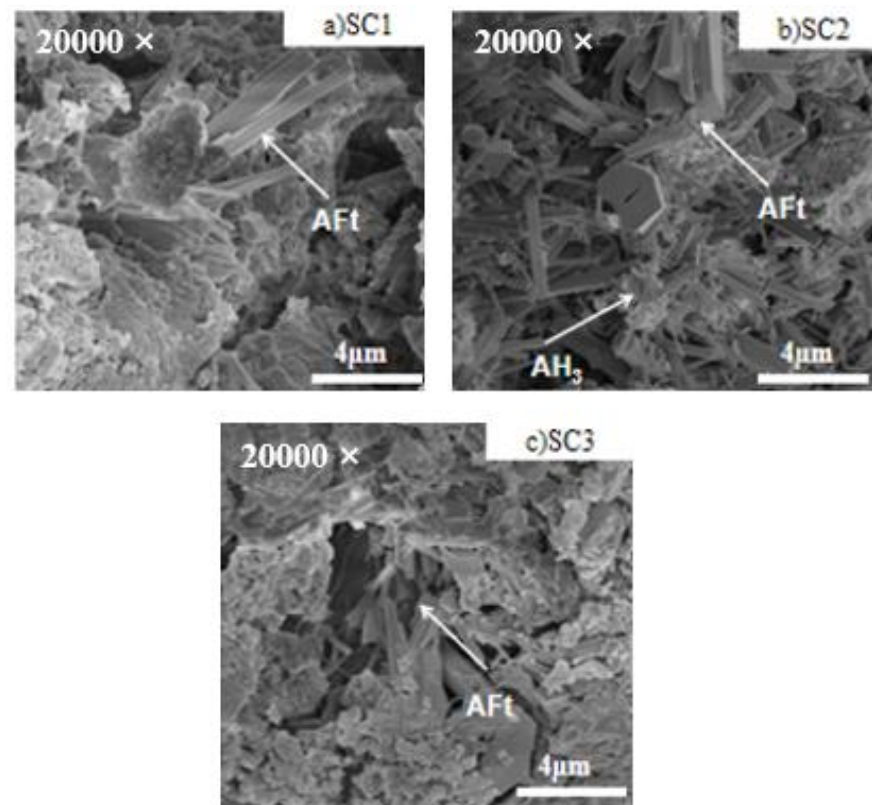


Figure 10. SEM-SE morphology of hydrated sample of SC1-SC3 at 3 days of age.

3.6. Porosity Analysis

The influence of porosity and pore size distribution on the strength of cement cannot be ignored and can laterally characterise the degree of hydration of the clinker minerals. The pore structure determines the denseness of cement-hardened slurries, and the pores are divided by the cause of their generation, with the pore types and pore size ranges shown in Table 5 [39–41]. Of these, gel pores and capillary pores are closely associated with the hydration products of the cement, while introduced pores and moulded pores are produced as a result of air-entraining agents or vibrations.

Table 5. Types and the ranges of pores in hardened pastes.

Pore Type	Aperture/nm	Causes
Gel pore	1–10 ²	Pores of gel-like substances in hydration products
Capillary pore	10 ² –10 ⁴	Pores between the larger size crystals in the hydration product
Introduced pore	10 ⁴ –10 ⁶	Pores introduced by air-entraining agents or aluminium powder during hydration
Forming pores	10 ⁶ –10 ⁷	Pore space due to the poor pounding of the paste

Figure 11 shows the pore size distribution of SC1-SC3 samples hydrated for 3 days. From the test results, the pore types of the samples were mainly gel pores; the median pore sizes of SC1 to SC3 were 16.4 nm, 11.9 nm, and 14.4 nm, respectively. Combined with the compressive strength of the cement test blocks, it can be found that the smaller the median pore size, the larger the compressive strength value of the test blocks; from SC1 to SC2 samples, the porosity decreased, and the compressive strength increased. The internal structure of the specimen gradually tended to become denser, and its contribution to the strength tended to increase. This was due to the gradual increase in AFt and AH_3 , which formed a structure that contributes to strength [42]. For the SC3 samples, the compressive strength decreased with increasing porosity. This indicates that the internal structure became loose when the C_3H_2 admixture was too high, which may have been related to the accumulation of AFt and the excess of C_3H_2 . More voids and unreacted gypsum were left in the hardened paste, adversely affecting the pore structure of the cement test blocks. The test results showed a good correspondence between porosity and compressive strength.

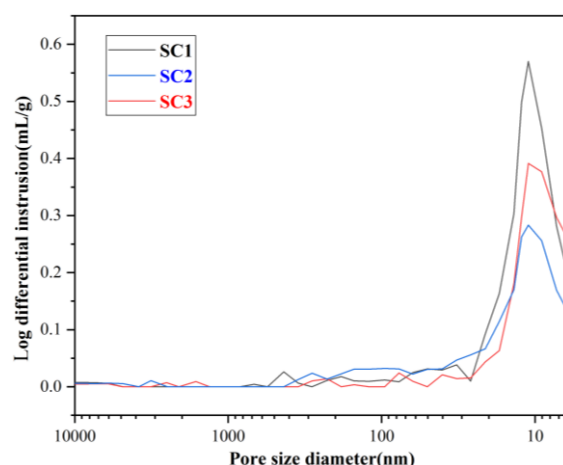


Figure 11. Pore size distribution of samples SC1-SC3 at 3 days of age.

4. Conclusions

This paper focused on calcium sulphoaluminate cement prepared from phosphogypsum, using two mineral admixtures, C_3H_2 and CH, to optimise the calcium sulphoaluminate cement-based materials. The development of compressive strength and changes in hydration products were studied, and the effects of clinker mineral composition and C_3H_2 and CH adding on the physical behaviour, hydration products, and microstructure of cement hardening pastes were analysed. The following conclusions were drawn from the above research process.

- (1) When C_3H_2 was added to the cementitious material, the early strength of the cement increased as the amount of C_3H_2 increased. The optimum admixture of C_3H_2/C_4A_3 was 1.5 mol. Adding CH decreased the cement's compressive strength and increased the paste's pH, which facilitated the development of the later strength. The optimum dose of CH/C_4A_3 was 0.5 mol.
- (2) The addition of C_3H_2 promoted the early hydration of C_4A_3 and formed more AFt. The amount of C_3H_2 incorporation and the AFt content were positively correlated. The incorporation of CH changed the hydration process. It inhibited the early hydration of C_4A_3 , and the hydration products appeared as AFm. With the increase in CH, the amount of AFt production became less, and the AFm content increased.
- (3) The addition of C_3H_2 influenced the microstructure of the matrix. With the increase in C_3H_2 , it was observed that the AFt crystals developed well, and the microscopic morphology changed from needle-rod to columnar or block. Excessive C_3H_2 caused AFt crystals to be stacked, not tightly cemented with AH_3 . At the same time, the matrix contained unreacted C_3H_2 , leading to an increase in pore size and porosity.

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