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Properties and Mechanism of Hydration of Fly Ash Belite Cement Prepared from Low-Quality Fly Ash

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Abstract: Fly ash belite cement (FABC) is predominantly composed of $\alpha'_{\rm L}$ -C₂S and C₁₂A₇. It is prepared from low-grade fly ashes by hydrothermal synthesis and low-temperature calcination methods. The formation, evolution process, and microstructure of FABC hydration productions were studied in this work, and the ultimate aim is to give a theoretical foundation and technological support for the application of the new cementitious material made of low-quality fly ash. The results showed that the optimal amount of gypsum was about 7% of cement by weight. The 3-day and 28-day compressive strength of cement pastes with 7% gypsum was 13.6 and 60.2 MPa, respectively. Meanwhile, the 28-day flexural and compressive strengths of mortars with 7% gypsum were 4.6 and 25.9 MPa, respectively. The early hydration heat release rate of this low-temperature calcined cement was higher compared with that of high-temperature calcined cement as Portland cement. FABC hydration pastes contained mostly C-S-H, ettringite (AFt), unreacted mullite, and quartz. It was significantly different from Portland cement in that no calcium hydroxide [Ca(OH)₂] was observed in the hydration products of different ages because all Ca(OH)₂ formed in the hydration reaction could react completely to generate AFt. The ratio of harmful pores (d \geq 50 nm) reached 55.04% after 3-day hydration. However, it decreased to 6.71%, which was lower than that of Portland cement pastes (35.72%) after 28-day hydration. In the later hydration period from 3 to 28 days, the strength developed rapidly, and a compact microstructure appeared in the hardened paste due to the presence of pores less than 20 nm in diameter.

Keywords: belite cement; gypsum; hydrothermal synthesis; pore structure

1. Introduction

Nowadays, the annual output of fly ash is approximately 600 million tons in China. A part of it obtained by the dry process has been basically applied in cement and concrete. However, still a lot of fly ash obtained by the wet process has not been employed in cement and concrete production due to its coarse particles, high carbon content, and low pozzolanic activity [1–4]. Accordingly, more than 1 billion of low-quality fly ash has been stockpiled, which not only occupies land but also pollutes the environment. Some recent studies applied ultrafine grinding to improve the activity of stockpiled high-carbon fly ash so as to meet the requirement of fineness and activity index of admixture in cement and concrete. However, this method could not decrease the content of carbon. Moreover, it had significant adverse impacts on the strength and frost resistance of concrete [5–9]. Therefore, the resource utilization of stockpiled high-carbon fly ash has been an urgent need.

Fly ash belite cement (FABC) is a low-carbon cement prepared from fly ashes by hydrothermal synthesis and low-temperature calcination methods. The basic composition of FABC is active dicalcium

silicate (2CaO·SiO₂; β -C₂S), calcium aluminate (12CaO·7Al₂O₃; C₁₂A₇), and some inert materials depending on the raw materials such as mullite, quartz, and iron oxide [10]. It has gained increasing attention from scholars because of much less CO₂ emission, low calcium oxide (CaO) content, and low heat of hydration. The hydrothermal synthesis and low-temperature calcination between 700 and 950 °C also improve the grindability of FABC and reduce energy consumption during preparation. Furthermore, this kind of cement can be synthesized from industrial wastes such as coal fly ash, coal gangue, and straw ash instead of natural quarried clay [11–14]. The high carbon content of stockpiled fly ash can provide energy for burning in the preparation of FABC. Hence, it is an effective way to comprehensively use the stockpiled high-carbon fly ash by preparing FABC.

The preparation methods of FABC are divided into two types based on different hydrothermal conditions of precursors [10,12]: the slurry-hydrothermal synthesis method and granule-hydrothermal synthesis method. In the slurry–hydrothermal synthesis method, precursors are prepared mainly by hydrothermal synthesis at more than 200 °C with a water-to-solid ratio of 5–10. However, higher water requirement and lower early-stage strength have been identified as problems in the FABC application. Guerrero et al. [5] and Goni and Guerrero [8] made a lot of effort to increase the content of hydraulic minerals by adding alkali activators in the preparation of precursors and reducing the water-to-cement ratio by adding a water-reducing agent in the preparation of cement pastes. Modified by 2% naphthalene water reducer, the 7-day compressive strength and the water requirement of FABC pastes increased by more than 40% and reduced by 15%, respectively. However, the 28-day compressive strength of mortars was lower than 20 MPa according to EN-196-2005, when the water-to-cement ratio dropped only from 1 to 0.85. FABC obtained by the slurry-hydrothermal synthesis method did not have better performance. On the contrary, in the granule-hydrothermal synthesis method, the hydrothermal synthesis temperature was lower than 100 °C. Some studies [15–17] suggested a hydrothermal synthesis method to synthesize belite cement, but the 28-day compressive strength of mortars prepared with this cement was lower than 20 MPa because the formation process of precursors was not activated by chemical activators. Previous studies [10,18] revealed that FABC was prepared from high-carbon, low-activity stockpiled fly ash by the granule-hydrothermal synthesis method. The 28-day compressive strength of mortars modified with 1% water reducer reached 30.2 MPa.

Recent studies focused mainly on raw materials such as coal fly ash, straw ash, and coal gangue, and the technology for preparing FABC [6,12]. They showed that fly ash (FA) and calcium oxide (CaO) as raw materials had a significant role in the preparation of FABC due to the composition of starting materials, fineness, and glass-phase content. The effects of temperature on hydrothermal synthesis, concentration of sodium hydroxide as an activator, reaction time, and conditions of calcination on the formation of FABC have been investigated. However, the hydration mechanism and characteristics of FABC are still rarely reported [19,20]. Hence, this study was performed to examine the hydration properties of FABC prepared from stockpiled high-carbon fly ash by the hydrothermal synthesis and low-temperature calcination methods.

2. Materials and Methods

2.1. Raw Materials

The FA was stored in the Xingtai Thermal Power Plant of Northern China. NaOH (Analytical Reagent, NaOH \geq 96.0%, Chron Chemicals, Chengdu, China) was used as an activator in the process of granule–hydrothermal synthesis. The preparation steps of FABC were as follows. First, FA, pure lime with 99 wt % CaO (Analytical Reagent, CaO \geq 98.0%, Chron Chemicals, Chengdu, China), and Na₂O (Na₂O was added as equivalent NaOH) at a ratio of 70:30:1 were mixed uniformly. Second, the mixtures were wound into a ball with the diameter ranging from 8 to 12 mm through a small disk granulator. Third, these granule specimens were hydrothermally treated at 90–100 °C for at least 12 h. Finally, all dried precursors were burned in a furnace in the following parameter settings: rate of temperature rise, 10 °C/min; final temperature, 800 °C; holding time, 1–1.5 h, and rapid

cooling. The residual over the 45-µm sieve in the clinker was less than 5.0%, and the density of the clinker was 2.82 kg/m³. Then, FABC was prepared by adding designed proportions of gypsum (Analytical Reagent, CaSO₄·2H₂O \geq 99.0%, Chron Chemicals, Chengdu, China). FABC was compared with Chinese P·I 42.5 cement, which was defined as reference cement (RC). ISO679-standard sands (Xiamen ISO Standard Sand Co.,Ltd, Xiamen, China) were used for testing the strength of cement mortars. The chemical composition of FA, clinker, and RC are given in Table 1.

Composition/Property	Fly Ash	Clinker	P·I 42.5 Cement (RC)
Chemical composition,			
wt %			
SiO ₂	49.21	32.94	22.04
Al_2O_3	29.46	19.68	4.76
Fe ₂ O ₃	4.36	3.80	3.10
CaO	2.26	36.87	64.5
MgO	0.80	0.82	0.92
TiO ₂	1.21	0.83	N/A
Na ₂ O	0.39	1.06	0.53
K ₂ O	0.28	0.71	0.32
SO_3	0.18	0.53	1.90
Loss	10.08	1.97	1.01
Density, g/cm ³	N/A	2.82	3.12
Blaine specific area, m ² /kg	438.3	585	332
Residual, >45 µm/wt %	2.4	4.5	6.2

Table 1. Chemical composition and physical properties of fly ash, clinker, and reference cement (RC).

The phase composition of the clinker under the above preparation conditions is shown in Figure 1. The clinker had α'_L -C₂S (d = 0.2730 and 0.2663 nm), C₁₂A₇ (2 θ = 18.0° and 34.0°), quartz (2 θ = 20.8° and 26.7°), and mullite (2 θ = 16.4° and 26.1°). These broader characteristic peaks of 2 θ from 32° to 36° demonstrated the lower crystallinity and smaller grain size of α'_L -C₂S compared with β -C₂S. It also proved that the hydration activity of α'_L -C₂S was higher than that of β -C₂S. However, gehlenite (2CaO·Al₂O₃·SiO₂; C₂AS, 2 θ = 18.0° and 34.0°) without any hydraulicity was created from CaO, SiO₂, and Al₂O₃ when the temperature exceeded 900 °C. With the increasing calcination temperature, the number of C₂AS increased gradually, while the content of β -C₂S and C₁₂A₇ decreased, resulting in lower hydration activity. For all these reasons, the proper calcination temperature of clinker ranged from 800 to 900 °C and effectively avoided the formation of C₂AS.



Figure 1. X-ray diffraction of belite cement clinker.

The microstructure of the clinker is shown in Figure 2. As shown in the figure, the clinker minerals were made of small particles, which were mostly less than 100 nm. Some high-porosity, irregular particles were also found. Figure 2b shows that the grain size of the clinker was less than 2 μ m. The combined analysis of the smaller particle size, looser structure, higher porosity, and crystal structure of $\alpha'_{\rm L}$ -C₂S and C₁₂A₇ revealed that this clinker had higher hydration activity than clinker calcined at a high temperature. In addition, unreacted mineral particles originating from the FA were observed. The porous particles increased the water requirement and hydration rate of the clinker while preparing cement paste, mortar, or concrete. The smaller grain sizes improved the grindability of all the clinkers, which reduced the energy consumption in the cement grinding process.



Figure 2. Scanning electron microscopy of belite cement clinker: (a) particles; (b) powders.

2.2. Preparation of Specimens

The porous particles increased the water requirement of the clinker when used in the preparation of pastes, mortar, and concrete. The FABC pastes with different contents of gypsum (w/c = 0.43) and Portland cement pastes with normal consistency (w/c = 0.28) were prepared, and $20 \times 20 \times 20$ mm³ cubic specimens were formed. FABC mortars were prepared with a water-to-cement ratio of 0.6, and $40 \times 40 \times 160$ mm³ specimens were formed with a sand-to-cement ratio of 3:1. The paste and mortar specimens were demolded after 24 h in a cement standard curing box with temperature $20 \ C \pm 1 \ C$ and relative humidity of 90% and then cured for different ages in water at temperature $20 \pm 1 \ C$. The strength development and hydration properties of FABC mortars were tested at the ages of 3, 28, and 90 days. The setting time and water requirement were tested from GB/T1346-2011, and strength was tested from GB/T17671-1999.

2.3. Methods

The x-ray diffraction (XRD) pattern, Fourier transform infrared spectrometer (FTIR), isothermal calorimetry result, scanning electron microscopy (SEM) image, and mercury intrusion porosimeter (MIP) of the hardened paste cured for 3 days, 28 days, and 90 days were recorded. The clinker and pastes were analyzed with an Isothermal Calorimetry (TAM-Air 8, TA Instruments, New Castle, DE, USA), XRD (Smart Lab 9kw, Rigaku, Tokyo, Japan), and FTIR spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) to determine the chemical composition of minerals and hydration products of different ages. Field emission SEM (Zeiss Sigma 15 kV, Germany) and MIP (Poremaster 60GT, Quantachrome Instruments, Boynton Beach, FL, USA) were used to characterize the morphology and pore structure.

3. Results

3.1. Effect of Gypsum Content on the Performance of FABC Pastes

The optimal amount of gypsum was investigated by observing the performance of pastes with different gypsum contents as 3%, 5%, 7%, and 10%; the results are shown in Table 2. As the gypsum content increased, the water requirement of cementitious materials decreased, and the setting time was slightly prolonged. In general, the setting time of FABC with different gypsum contents was very short. Even for the cement with a gypsum content of 10%, the initial setting time was only about 25 min, and the final setting time was only about 40 min. The main reason was that the activity and content of $C_{12}A_7$ in the clinker were higher than those of C_3A in Portland cement, and the reaction speed was very high. The water requirement of FABC was more than that of Portland cement, while the water requirement of RC was 28.6%. FABC had a higher porosity and specific surface area. Further, the clinker reacted immediately with water, which had a "drying" effect on the slurry and further increased the water requirement. The optimal amount of gypsum was about 7% of cement by weight. Meanwhile, the 3-day and 28-day compressive strength of cement pastes was 13.6 MPa and 60.2 MPa, respectively. This was because gypsum provided enough ettringite for covering and isolating the clinker particles, thus having a retarding effect on cement hydration and the setting of hydraulic minerals. In summary, the optimal amount of gypsum was about 7% of cement by weight.

No.	Gypsum (%)	Water Requirement (%)	Setting Time (min)		Compressive Strength (MPa)	
			Initial	Final	3-day	28-day
1	3	43.9	16	22	10.7	36.3
2	5	43.1	18	25	12.7	42.0
3	7	42.5	20	30	13.6	60.2
4	10	41.0	25	40	11.4	53.2

Table 2. Performance of fly ash belite cement (FABC) with different gypsum contents.

The mechanical properties of mortars with different gypsum contents were studied at the same time, and the results are shown in Figure 3. The results showed that the compressive strength and flexural strength were the highest when the gypsum-adding rate increased to 7%. The experimental results showed that the 3-, 28-, and 90-day compressive strengths of mortars reached 6.0, 25.9, and 28.4 MPa, respectively. In addition, the 3-, 28-, and 90-day flexural strengths of mortars reached 1.6, 4.6, and 5.8 MPa, respectively. The setting time of FABC was very short in the early stage because gypsum, as a sulfate admixture, promoted the reaction of alumina phase with Ca(OH)₂ to generate a more aciculate ettringite $(AFt, 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$ crystal and increased the strength at the early ages, which was stable at the later ages. However, the compressive and flexural strengths increased initially and then decreased with the increase in gypsum doses. The main reasons for this change in strength were as follows. On the one hand, AFt formed from the aluminate phase, Ca(OH)₂, and gypsum filled the porous space, which together with C-S-H gels shortened the setting time and improved the early strength. Mostly calcium aluminate hydrates, such as C_3AH_8 and C_4AH_{16} , were observed, without significant AFt using lower contents of gypsum. On the other hand, the extremely high content of gypsum in the clinker did not support the development of its later-stage strength due to the lack of hydraulic clinker. Especially, it resulted in expansion damage through delayed ettringite (DEF) formation. To summarize, the numerical results indicated that the optimum content of gypsum in FABC was 7%.



Figure 3. Strength of mortars with different gypsum contents.

3.2. Heat of Hydration of Cement Pastes

The change in the hydration heat of FABC and P·I 42.5 with time was analyzed using the isothermal calorimeter. The heat evolution rates and cumulative hydration heat of different types of cements are shown in Table 3 and Figure 4. The first heat peak of FABC appeared after 47 min. Meanwhile, the heat evolution rate reached 0.02685 W/g, which was three times as large as that of P·I 42.5. However, the heat evolution rate of the second heat peak reached 0.00612 W/g following the first heat peak after 360 min; different from P·I 42.5, it had shorter intervals. FABC had the first heat peak because of $C_{12}A_7$ hydration and then the second heat peak because of ettringite (AFt, 3CaO·Al₂O₃·3CaSO₄·32H₂O) formation and C₂S hydration.

First Evolution Peak Second Evolution Peak 7-day Cumulative No. **Heat Evolution** Heat Evolution Hydration Heat (J/g) Time (min) Time (min) Rate (W/g) Rate (W/g) FABC 101.16 47 0.02685 0.00612 360 0.00947 0.00293 308.11 46 2562 RC 0.030 400 (b) RC (a) • FABC RC Cumulative hydration heat (J/g) 0.025 - FABC Heat evolution rate(W/g) 300 0.020 250 0.015 200 150 0.010 100 0.005 0.00 40 50 60 Time (h) Time (d)

Table 3. Heat evolution characteristics of FABC and RC.

Figure 4. Heat evolution characteristics of FABC and RC: (a) Heat evolution rate; (b) Cumulative hydration heat.

FABC released heat more rapidly in the early stage of hydration compared with P·I 42.5, and the total heat of 7 days was less than 102 J/g, which was only one third of the P·I 42.5 heat. The hydration heats of FABC in 1 day reached about 70.5% of the total heat of 7 days and were then up to 81.6% 3 days later. However, the hydration heat of P·I 42.5 in 3 days reached 91% of the 7-day total heat, which was more than that of FABC release. The results showed that the exothermic reaction mostly happened on the first day of FABC hydration; however, it occurred on the third day of P·I 42.5 hydration. This was

because $C_{12}A_7$ released a lot of heat in a short time and accelerated the setting of FABC in hydration because of high activity in the clinker and porous structure.

3.3. Composition of FABC Hydration Products

The FTIR patterns of FABC pastes hydrated for different ages are shown in Figure 5. The results showed that the wavenumbers and curves of 3-, 7-, 28-, and 90-day pastes were essentially the same, indicating that the hydration products did not change with the development of the hydration process. The infrared spectra of pastes of four ages showed the characteristics of hydration products in wide absorption bands. This was largely due to two reasons [19]: first, the hydration products of FABC had a lower degree of crystallization, resulting in a larger change in the vibration frequency of groups; second, it was a superposition of infrared spectroscopy from various hydration products in the similarity region.



Figure 5. Fourier transform infrared spectrometer (FTIR) patterns of pastes hydrated for different ages.

The strong bands at 872 and 964 cm⁻¹ were because of the asymmetrical stretching vibration (v_3) of $[SiO_4]^{2-}$ and $[AlO_4]^-$ groups from C-S-H and C-A-H gels, which had a disordered structure. $[CO_3]^{2-}$ groups were observed at 1430 and 872 cm⁻¹ assigned to the asymmetrical stretching vibration (v_3) and out-of-plane bending vibration (v_2) , respectively, indicating that carbonation easily occurred in hydration products. Another strong band at 3440 cm⁻¹ of crystal water was due to the asymmetrical stretching vibration (v_3) . Different from most ordinary Portland cement pastes, the band at 3640 cm⁻¹ of the OH⁻ group due to the asymmetrical stretching vibration (v_3) in portlandite was never found. The possible reason was that all Ca(OH)₂ was consumed in forming AFt according to Equation (1), until it was completely absorbed. With the increase in curing time, the bands at 900–1100 cm⁻¹ of [SiO₄]²⁻ groups were found to shift to higher frequencies, suggesting that the degree of silicate polymerization increased with the hydration time. Therefore, it was predicted that the Si-O bonds of Q_2 in C-S-H gels increased, and more hydration products were generated.

XRD patterns of FABC pastes hydrated for 3, 7, 28, and 90 days are shown in Figure 6. After 3 days, C-S-H gels ($2\theta = 28-30^{\circ}$) and AFt ($2\theta = 9.2^{\circ}$) were generated in large numbers. In addition, unhydrated α'_{L} -C₂S ($2\theta = 32-34^{\circ}$), unreacted quartz, mullite, and AFt were found in FABC pastes. After 7-day curing, the diffraction peaks of AFt ($2\theta = 9.2^{\circ}$) became sharper, proving that gypsum participated in the reaction sustainably. After 28-day curing, these products still existed as previously generated. With the increasing age, the intensity of the characteristic diffraction peaks of AFt was enhanced obviously. At the age of 90 days, α'_{L} -C₂S almost disappeared, the content of AFt had no significant change, and calcium carbonate was formed by carbonization reaction. In addition, no Ca(OH)₂ was found in

this hydration product on analyzing the XRD patterns because α'_L -C₂S in the clinker contained a low content of CaO and Ca(OH)₂ completely reacted to form AFt. Finally, Equation (1) was as follows.

$$12\text{CaO·7A}l_2\text{O}_3 + 9\text{Ca(OH)}_2 + 21\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 7(3\text{CaO·A}l_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O})$$
(1)

Figure 6. XRD patterns of pastes hydrated for different ages.

3.4. Microstructure of FABC Hydration Products

SEM images of FABC pastes hydrated for different ages are shown in Figure 7. After 3-day curing, some C-S-H gels and AFt were found distributed on the surface of unreacted clinker and mullite in the pastes with flocculent and loose microstructure, as shown in Figure 7a. A remarkable initial strength was achieved by the hydration process because the hydration rate of $\alpha'_{\rm L}$ -C₂S was higher than that of β -C₂S obtained at 1200 °C in Portland cement.



Figure 7. SEM images of pastes hydrated for different ages: (a) 3 days; (b) 28 days; (c) 90 days.

Subsequently, a large number of pores and fractures were formed after drying because of the higher water requirement. The hardened paste was cured for 28 days, as shown in Figure 7b. The main hydration product had mostly a network structure. In addition to the high water requirement, it had a low density of C-S-H gels mostly distributed in layers due to more porous particles in clinker and larger void space in the pastes for hydration to proceed. These very fine crystallites of AFt with micro-expansion filled pores during hydration and reduced the porosity and shrinkage ratio. Thus, a higher mechanical performance was achieved. Figure 7c shows the SEM image of the hardened paste cured for 90 days. In the later hydration period, the more compact microstructure appeared in the hardened paste, and the number of large pores reduced obviously. It also proved that the long-term strength sustained growth with a compact structure from 28 to 90 days.

3.5. Porosity of Hydration Products

The porosity analysis of FABC and RC pastes hydrated for different ages is shown in Figure 8. The cumulative porosity analysis revealed that the porosity of FABC pastes hydrated for 3, 28, and 90 days was 41.64%, 34.22%, and 33.16%, respectively, as shown in Figure 8a. At the same age, the porosities of RC pastes were 23.15% and 16.60%, which were lower than that of FABC, indicating that the high porosity was the main cause of low early strength of FABC pastes. The pore radius of RC pastes dropped from 56.16 to 45.10 nm in 3–28 days, whereas the pore radius of FABC paste dropped from 58.83 to 25.12 nm. It showed that the most probable pore radius of RC was more than 1.8 times that of FABC pastes in 28-day curing. The results showed that at early ages, the weaker mechanical properties of FABC hydration pastes were related to its loose microstructure and high porosity. From 3 to 28 days, the curing ages led to the thinning of pore size, compaction of hydration products, and high hydration degree, resulting in the improvement of mechanical properties of FABC pastes.



Figure 8. Cumulative porosity (a) and pore size distribution (b) of pastes hydrated for different ages.

Similar to Portland cement pastes, the pastes of FABC had a heterogeneous and multiphase structure; the pores were divided into gel pores, micro pores, and transitional pores. The size distribution of pores could be graded according to the effect of pores on pastes. It was divided into four parts: (I) diameter < 20 nm, harmless pores; (II) 20–50 nm, less harmful pores; (III) 50–200 nm, harmful pores; and (IV) > 200 nm, more harmful pores. Generally, the less the harmful pores (d > 50 nm), the better the mechanical properties of FABC pastes. Hence, the percentage of harmful pores (d > 50 nm) in pastes described the effect of pore structure characteristics on strength. The results are shown in Figure 8 and Table 4. The results indicated that the ratio of harmful pores was up to 55.04% at the age of 3 days. Then, after 28 days, it dropped to 6.71%, which was lower than 35.72% of RC pastes. In conclusion, although the FABC pastes had high porosity, the ratio of harmful pores with a diameter of larger than 50 nm dropped obviously with curing ages. A large number of pores were less than 20 nm diameter,

which was less harmful to the microstructure of pastes. Therefore, the harmful effect of high porosity on strength reduced markedly.

Sample	Porosity (%)	Most Probable Pore Radius (nm)	Pore Size Distribution (%)			Percentage of Harmful	
			d < 20 nm	20–50 nm	50–200 nm	d > 200 nm	Pores >50 nm (%)
FABC-3d	41.64	58.83	12.60	32.36	46.41	8.63	55.04
FABC-28d	34.22	25.12	43.20	50.09	1.81	4.90	6.71
FABC-90d	33.16	20.24	56.22	36.49	2.70	4.59	7.29
RC-3d	23.15	56.16	23.70	23.91	41.76	10.63	52.39
RC-28d	16.60	45.10	28.61	57.13	27.12	8.6	35.72

 Table 4. Pore structure parameters of different pastes.

4. Discussion

The results indicated that FABC was hydrated continuously during the investigation. The significant increase in strength between 3 and 28 days (Figure 3) might be due to the combined effect of two factors.

4.1. Hydration Activity of α'_L -C₂S in FABC Pastes

Compared with C₂S usually synthesized at higher than 1300 °C, the highly active C₂S (α'_L -C₂S) synthesized at 800 °C had smaller grains, larger specific surface area, higher porosity, higher hydration speed, and smaller later strength advantage. The highly active C₂S synthesized at a low temperature was responsible for the relatively high strength of fly ash belite cementitious material. However, the early strength development of FABC pastes was still slow. Especially, the early strength development from 1 to 3 days was slow. Hence, the early activity of α'_L -C₂S was far lower than that of C₃S in Portland cement [21–23]. The analysis of porosity and microstructure showed that the low strength of FABC pastes was smaller than that in Portland cement pastes, the harmful influence of porosity was more than that in Portland cement pastes because of high porosity.

4.2. Hydration Mechanism of α'_L -C₂S -C₁₂A₇-CaSO₄-System

The hydration products of α'_L -C₂S single minerals were C-S-H gels and Ca(OH)₂, and the hydration products of the α'_L -C₂S-C₁₂A₇-CaSO₄ system were C-S-H gels, AFt, and C₃AH₆. The coexistence of CaSO₄ and C₁₂A₇ promoted the hydration of C₂S, This was because the hydration of C₁₂A₇ released Al(OH)⁴⁻, which reacted with Ca(OH)₂ to form C₃AH₆, thus reducing the concentration of Ca²⁺ and accelerating the hydration of α'_L -C₂S. In the presence of CaSO₄, SO₄²⁻ combined with Ca²⁺ and Al(OH)⁴⁻ in the liquid phase to form ettringite. It reduced the content of hydrated calcium aluminate and Ca(OH)₂, accelerating the hydration of α'_L -C₂S further. It indicated that CaSO₄·2H₂O changed the hydration products of C₁₂A₇ and improved the hydration degree of FABC to a certain extent.

Hence, the coexistence of CaSO₄·2H₂O and C₁₂A₇ accelerated the hydration of α'_L -C₂S [24–26]. Clinker with a porous and loose structure had a high water requirement, which also resulted in the poor strength properties of FABC hydration pastes. FABC and Portland cement can be added to the composite to improve the hydration degree and strength of pastes, while Portland cement provided the alkaline environment and accelerated the hydration of FABC pastes. This was a very good and effective way to reduce the porosity influence on FABC, protect clay resources, and improve the utilization rate of low-quality fly ash.

5. Conclusions

This study focused on the hydration properties of FABC clinker predominantly composed of α'_L -C₂S and C₁₂A₇, which was prepared from stockpiled FA and lime. Some conclusions and recommendations based on the experimental results were as follows.

(1) When the dosage of gypsum was 7%, the compressive and flexural strengths of FABC mortars after 3, 28, and 90 days were the highest. Therefore, the optimum dosage of gypsum in FABC was 7%.

(2) Mostly C-S-H, AFt, mullite, and quartz were found in hydration products with no Ca(OH)₂. This was principally because all the Ca(OH)₂ generated from the hydration of α'_{L} -C₂S reacted to form AFt.

(3) FABC pastes had higher porosity and lower strengths compared with RC pastes at early ages, which was due to a high water requirement and small particle size of clinker. However, the ratio of harmful pores ($d \ge 50$ nm) decreased from 55.04% to 6.71% during the hydration period from 3 to 28 days. It was concluded that pores less than 20 nm in diameter were advantageous in improving the strengths and density of fly ash belite cement mortars rapidly at later ages.

Producing FABC by low-quality fly ash is believed to be a promising way to resourcefully utilize large amount of fly ash, and the long-term strength development can be found grow rapidly during 3 to 28 days. It can be predicted that FABC has rapid setting and hardening, good resistance to sulfate attack because of low $Ca(OH)_2$ content, and it is suitable for underground, underwater, or marine engineering, especially for projects requiring rapid construction or repair. Future work will focus on durability and composite cement. The working performance, mechanics performance, and durability of composite cement compounded with FABC and Portland cement will be studied in the future.

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