

Preparation of Fluorogypsum Based Cementitious Material

Yiming Niu, Shiying Chen

College of Resources and Environment, Henan Polytechnic University, Jiaozuo 454003, China

ABSTRACT

In order to realize the resource utilization of fluoropygite, the gelling material was prepared by using fluoropygite, fly ash and calcium carbide slag as composite raw materials. The optimal ratio was optimized by single factor test and orthogonal test, and the hydration mechanism and curing effect of fluoride ion were studied. The results show that the optimal ratio of strength for 3 days is fly ash: fluoropyssum: calcium carbide slag = 50:30:20, 7 days the optimal ratio of strength is fly ash: fluoropyssum: calcium carbide slag = 50:25:15, 28 days the optimal ratio of strength is fly ash: fluoropyssum: calcium carbide slag = 60:30:15. By XRD and SEM analysis, the addition of calcium carbide slag has a certain curing effect on fluorine ions in fluoropogon.

KEYWORDS

Fluorogypsum; Single factor experiment; Orthogonal experiment

1. INTRODUCTION

Fluogypsum is a kind of solid waste produced when sulfuric acid and fluorite are used to produce hydrofluoric acid. It is mostly white powder, mainly composed of anhydrous calcium sulfate [1, 2], and contains a small number of impurities such as silicon, aluminum, iron and potassium. According to statistics, the generation of 1 t hydrofluoric acid will produce 3 to 4 t of fluorine gypsum [3], and China's annual output of fluorine gypsum is as high as more than 2 million tons [4]. At present, the treatment method of fluorogypsum is simply landfill after treatment or directly sent to the slag field area for storage. Such traditional method will not only pose a huge threat to the surrounding environment and human health [5], but also bring relatively large economic pressure to the development of enterprises.

In order to solve the resource utilization of fluorgypsum, domestic and foreign scholars have carried out a series of studies. At present, the comprehensive utilization of fluorgypsum is mainly applied to cement retarder [6, 7], carbon fixation technology [8], and building materials [9, 10]. Yasser Bigdeli et al. [11] used PH-regulated fluorogypsum, fly ash and Portland cement to study the effects of setting time, density, voidage and curing time on strength and volume expansion to prepare concrete materials. The results show that the proposed fluorogypsum based admixture is a promising low-cost concrete class material for outdoor and underwater construction applications. M.p.uzmina et al. [12] used Portland cement clinker, fly ash, gypsum or fluorogypsum to replace cement, and confirmed the feasibility of using fluorogypsum to replace natural gypsum in the cement production process from the aspects of raw material fineness, setting time, compressive strength, packing density and so on. Crystal optics studies have demonstrated the role of fluorogypsum in the formation of cement stone and its role in the setting of cement slurry. The exact amount of fluorogypsum when grinding cement clinker was determined. Qin Haizhong et al. [13] carried out an experimental study on the ratio of fluorogypsum, waste rock, fly ash, quicklime and additives to a new type of fluorogypsum based paste filling material, and analyzed its macro and micro structure. The results

showed that when waste rock was 1 000 g, fluorogypsum 300 g, fly ash 400 g, and quicklime 70 g, The pressure of fluorogypsum base paste can reach 6 ~ 7 MPa. YAO Yan [14] et al. modified the waste fluorogypsum and used it as a cement retarder, and the results showed that the basic parameters of the performance after the improvement had been greatly improved. The flexural strength and compressive strength of modified fluorogypsum are roughly equivalent to that of natural gypsum. As a cement retarder, its setting time, stability and SO₃ content all meet the national standards.

In this paper, industrial waste fly ash, fluorogypsum and calcium carbide slag were used as raw materials to prepare cementing materials. The influence of each raw material content on cementing system was studied, and the optimal ratio of cementing system was obtained through orthogonal experimental design optimization. By means of XRD, SEM and other analysis methods, the hydration mechanism of composite cementing materials and the curing effect of fluoride ions were investigated. In order to solve the harm caused by the accumulation of industrial waste residue to the environment, reduce carbon dioxide emissions, help to achieve "carbon neutrality, carbon peak" with high economic and social benefits, contribute to the resource utilization of fluorogypsum.

2. EXPERIMENT

2.1. Raw Material

The fluorine gypsum in this experiment was taken from Jiaozuo Polyfluorine Chemical Co., LTD., and its main phase was anhydrous calcium sulfate. Its PH value was determined to be 1.9 and it was strongly acidic. The fly ash used in the experiment is commercially available secondary fly ash, and its main components are SiO₂ and Al₂O₃. Calcium carbide slag from Henan Energy and Chemical Group Hebi Coal Chemical Co., LTD., its main component is Cao. The composition of each raw material is shown in Table 1.

Table 1. Chemical composition of raw materials (w/%)

Type	SO ₃	CaO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	K ₂ O	Fe ₂ O ₃	SrO
flyash	2.27	3.93	49.67	36.78	0.09	1.21	4.08	0.14
fluorgypsum	57.62	41	0.892	0.152	0.02	0.02	0.09	0.02
carbide slag	2.89	91.27	3.94	-	-	0.23	0.28	0.08

3. EXPERIMENTAL RESULT

3.1. Single Factor Experiment

In order to find out the best content between fly ash, fluoropygite and calcium carbide slag in composite cementing material, so as to achieve the maximum strength of FFC cementing material, the bending and compressive relations of different ratios and different ages were determined according to GB/T17671-1999 "Cement mortar Strength Test Method (ISO)". Under the total dosage of 1000g and water-binder ratio of 0.4, the flexural strength and compressive strength of each ratio for 3 days, 7 days and 28 days were determined by single factor experiment.

Figure 1 uses fly ash as variable and fixed mass ratio of fluorogypsum and calcium carbide slag to study the influence of fly ash admixture on bending and compressive strength of cementing system at different curing ages. It can be seen from Fig. 1 (a) that with the increase of fly ash production, the 3d, 7d and 28d bending strength of the fluoropyg-based cementable material presents a change law of first increasing and then decreasing. When the fly ash content is 56%, the 3d, 7d and 28d bending strength of the fluoropyg-based cementative material is 0.56MPa(3d) 0.83MPa(7d) 2.12MPa(28d), and when the fly ash content is 60%, the 3d, 7d and 28d bending strength of the fluoropyg-based

cementative material reaches the maximum value. They were 0.53MPa(3d), 0.87MPa(7d) and 2.18MPa(28d), respectively. At this time, there was no significant change in the bending strength of the two groups with different proportions, and the difference was less than 5%.

It can be seen from Fig. 1 (b) that with the increase of the amount of fly ash, the 3d strength of the cementing material shows a decreasing trend. When the curing time is 7 days, there is no obvious change rule of the gelling system. When the curing time was 28d, the compressive strength showed a trend of increasing first and then decreasing, and the peak value of fly ash admixture appeared at 60%. As the amount of fly ash continued to increase, the compressive strength of the cementing material decreased sharply. According to the influence of fly ash on the early and late strength of the cementing system, when the fly ash admixture is 60%, the strength of the cementing system reaches the maximum at different ages, which are 1.89MPa(3d), 2.55MPa(7d) and 6.53MPa(28d), respectively.

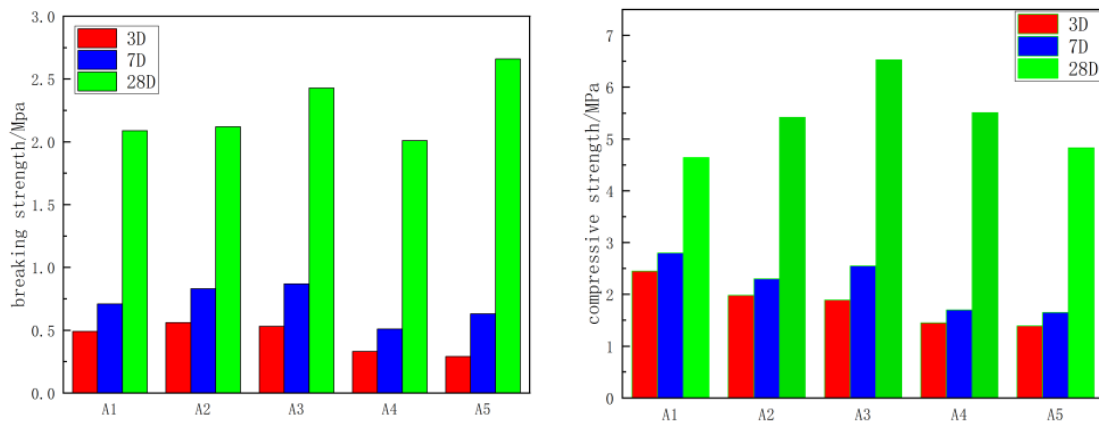


Figure 1. Single factor data graph with fly ash as variable (a left figure: flexural strength; b Right picture: compressive strength)

This is mainly because when the amount of fly ash is very small, with the increase of the amount of fly ash, the number of hydration products such as calcium silicate and calcium sulfoaluminate generated by the hydration reaction of fly ash under the activation of $\text{Ca}(\text{OH})_2$ and fluorogypsum also gradually increases, so that the strength of FFC gelling materials continues to increase. When the amount of fly ash increased to a certain value, the number of hydration products reached the highest, and the strength of FFC cementing material reached the maximum. Later, as the amount of fly ash continues to increase and the amount of fluorogypsum continues to decrease, the porosity of FFC cementing material system will gradually increase. Although the number of hydration products will not decrease at this time, the strength of FFC cementing material will also decrease.

In Figure 2, the mass ratio of fixed fluorogypsum and calcium carbide slag was used as variable to study the influence of fluorogypsum admixture on the bending and compressive strength of the cementing system at different curing ages. As can be seen from Figure 2(a), when the fluorogypsum is 22%, the flexural strength of different ages is the lowest, and with the increase of the fluorogypsum content, the flexural strength also increases. When the fluorogypsum content is 27% and 33%, the flexural strength reaches the maximum value, and the difference of flexural strength of different ages of the two ratios is less than 5%. It shows that the increase of content of fluorogypsum is beneficial to the flexural strength of the gelling system. When the content of fluorogypsum continues to increase to 39%, the proportion of fly ash and calcium carbide slag is the smallest, and the bending strength shows a slow decline trend.

As can be seen from Fig. 2 (b), with the increase of the dosage of fluorogypsum at the curing age of 3 days, the 3d strength of the cementing material first increased, then decreased and then increased slowly, with no significant difference from 2.5MPa to 2.53MPa. When the curing time is 7 days, the strength of the cementing material reaches the maximum value when the content of fluorogypsum

is 27%. When the curing time was 28 days, the compressive strength showed a trend of first increasing and then slowly decreasing, and the peak value of the fluorogypsum admixture appeared at 27%. When the dosage of fluorogypsum continued to increase, the strength of the cementing material showed a slow decreasing trend. When fluorogypsum is 60%, the strength of the cementation system reaches the maximum at different ages, which are 2.74MPa(3d), 2.85MPa(7d) and 6.53MPa(28d), respectively.

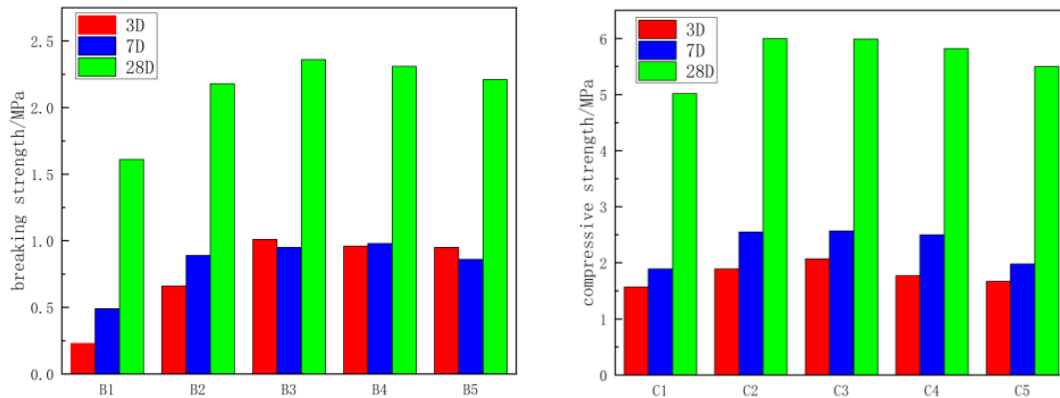


Figure 2. Single factor data graph with fluorogypsum as variable (a left figure: flexural strength; b Right picture: compressive strength)

With the increase of fluorine gypsum production, the gelling material exhibits higher flexion and compressive strength, which is because the addition of gypsum promotes the hydration of the gelling system. In fluorine gypsum and fly ash, Si and Al form ettringite crystals under the action of $\text{Ca}(\text{OH})_2$. When fluorine gypsum is added too much, the content of fly ash decreases, while the content of Si and Al is insufficient. Excessive fluogypsum mainly plays the role of filling, and the formation of ettringite and C-S-H gel decreases, and the bending and compressive strength decreases accordingly. This indicates that when the amount of fly ash and calcium carbide slag is constant, the amount of fluogypsum in the cementing material does have a proportional relationship to maximize the strength of the cementing material.

Figure 3 is the mass ratio of calcium carbide slag as variable, fixed fly ash and fluorgypsum, to study the influence of calcium carbide slag admixture on the compressive strength of the cementing system at different curing ages. It can be seen from Figure 3 (a) that with the increase of calcium carbide slag content, the bending strength also increases. When the content of calcium carbide slag increases to a certain value, the bending strength reaches the maximum value, and then gradually decreases with the continuous increase of calcium carbide slag. When the calcium carbide slag content is 20%, the maximum flexural strength for 7 days and 28 days is 1.04MPa and 2.21MPa, respectively. When the calcium carbide slag content is 27%, the maximum flexural strength for 3 days is 0.8MPa. As can be seen from Fig. 3 (b), with the continuous increase of calcium carbide slag content, the 3-day strength reaches the maximum when the calcium carbide slag content is 27%. When the calcium carbide slag content is 20% and 27%, the 7-day compressive strength reaches 2.55MPa and 2.57MPa, respectively. On the basis of this content, the 28-day compressive strength is 6.0MPa and 5.99MPa, and the compressive strength at this time is the maximum.

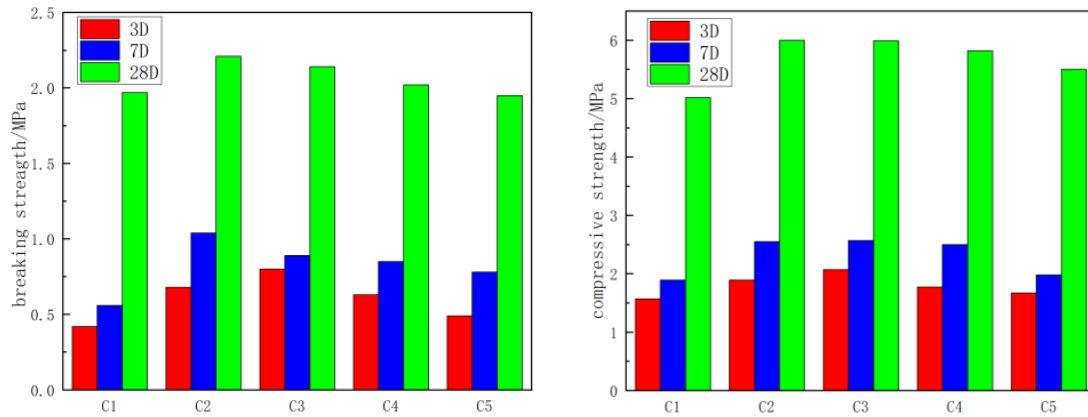


Figure 3. Single factor data graph with calcium carbide slag as variable (a left picture: flexure strength; b Right picture: compressive strength)

This is mainly because calcium carbide slag is mainly composed of CaO, which provides an alkaline environment for the reaction system, stimulates the activity of fly ash during the reaction process, releases a large amount of heat to promote hydration reaction, and generates Aft and C-S-H gels, which greatly improves the densification of the gelling system and further improves the strength. However, with the increase of calcium carbide slag content, the reaction system will be strengthened. If the concentration of (OH-) in the system is high, the rapidly generated hydration products will form a protective film on the surface of fly ash particles, preventing the hydration of fly ash. Excessive calcium oxide in calcium carbide slag will react with water to generate a large amount of Ca (OH)₂, prompting the material to constantly form Aft. Excessive Aft will lead to the expansion and cracking of the gelling system, and eventually lead to the strength of the test block.

3.2. Orthogonal Experiment

According to the single factor test results, considering the influence of each dosage on the bending compressive strength, a three-factor, three-level orthogonal design (L₉(3³)) was selected for the test. The design principle is shown in the figure. The three factors are fly ash content (A), fluogypsum content (B) and calcium carbide slag content (C), and the fixed water-binder ratio (W/B) is 0.4. Table 2 is the factor level table.

Table 2. Level table of factors

level	Horizontal correspondence value		
	A	B	C
1	50	20	15
2	55	25	20
3	60	30	25

According to the level values shown in Table 2, the test blocks of the fly-ash - fluoropygsum - calcium carbide slag composite cement material were cured at room temperature respectively in accordance with the preparation process until the specified age period (3d, 7d, 28d), and the uniaxial flexural and compressive strength of the composite material was measured. The test results are shown in Table 3.

Table 3. Orthogonal experiment results

Serial number	adulterate amount/%			rupture strength/MPa			compressive strength/MPa		
	FA	FG	CS	3 day	7 day	28 day	3 day	7 day	28 day
A1	50	20	15	0.9	2.10	5.78	2.38	5.34	12.01
A2	50	25	20	1.02	1.79	5.41	3.05	5.16	12.06
A3	50	30	25	1.09	1.8	5.05	3.16	5.07	11.41
A4	55	20	20	0.79	1.88	5.62	2.25	4.69	12.52
A5	55	25	25	0.86	1.86	4.83	2.35	5.17	11.21
A6	55	30	15	0.96	1.95	5.59	2.47	5.05	13.22
A7	60	20	25	0.71	1.53	4.84	1.83	4.22	11.17
A8	60	25	15	0.86	2.02	6.07	2.41	5.53	13.25
A9	60	30	20	0.88	1.96	5.54	2.51	4.98	13.15

3.2.1. Range analysis

The range analysis of the compressive strength data of the fly-ash - fluoropergypsum - calcium carbide slag composite cementative material at different ages (3 d, 7 d, 28 d) was conducted, and the results were shown in Table 4. The greater the range value, the greater the influence of this factor on the strength. The main order of the influence of each factor on the 3D compressive strength was the content of fly ash > the content of fluoropergypsum > the content of calcium carbide slag. The corresponding range values are 0.617, 0.563 and 0.183, respectively, indicating that fly ash is the key factor affecting the early strength of composite materials. The order of the influence of all factors on the 7-day compressive strength is the content of fluoropergypsum > calcium carbide slag > fly ash content, indicating that the content of fluoropergypsum is the most important factor affecting the medium-term strength in the test when the curing period is 7 days, and the corresponding ranges are 0.53, 0.487 and 0.280 respectively. The order of the influence of all factors on the 28-day compressive strength is the content of calcium carbide slag > fluorogypsum content > fly ash content, indicating that the content of calcium carbide slag is the most important factor affecting the late strength of the system, and its range is 1.56, 0.69, 0.52, respectively.

Table 4. Range analysis

Type of range	Factor	A	B	C	Significance
R3d/MPa	k1	2.863	2.150	2.420	A>B>C
	k2	2.357	2.603	2.603	
	k3	2.247	2.713	2.443	
	Range	0.617	0.563	0.183	
	optimal level	A1	B3	C2	
R7d/MPa	k1	5.190	4.750	5.307	B>C>A
	k2	4.970	5.287	4.943	
	k3	4.910	5.033	4.820	
	Range	0.280	0.537	0.487	
	optimal level	A1	B2	C1	
R28d/MPa	k1	12.01	11.90	12.83	C>B>A
	k2	12.32	12.35	12.76	
	k3	12.52	12.59	11.26	
	Range	0.52	0.69	1.56	
	optimal level	A3	B3	C1	

3.2.2. Analysis of variance

The strength of samples at different ages was analyzed by variance, and the results were shown in Table 5. According to the results of variance analysis, the content of each material has a certain influence on the strength of the composite. The order of influence on the 3-day compressive strength is the content of fly ash > the content of fluorogypsum > the content of calcium carbide slag > the content of fly ash; the order of influence on the 7-day compressive strength is the content of fluorogypsum > the content of calcium carbide slag > the content of fly ash; the order of influence on the 28-day compressive strength is the content of calcium carbide slag > the content of fluorogypsum > the content of fly ash. The results of variance analysis and range analysis of each factor are consistent.

Table 5. Analysis of variance

Item	Factor	DF	Adj SS	Adj MS	F	P	Significance
3day	A	2	0.649	0.325	10.13	0.09	A>B>C
	B	2	0.535	0.267	8.35	0.107	
	C	2	0.060	0.030	0.93	0.517	
7day	A	2	0.130	0.065	0.62	0.629	B>C>A
	B	2	0.433	0.216	2.05	0.328	
	C	2	0.384	0.192	1.82	0.355	
28day	A	2	0.406	0.203	3.39	0.228	C>B>A
	B	2	0.744	0.372	6.22	0.139	
	C	2	4.679	2.339	39.11	0.025	

According to the results of range and variance analysis, the optimal 3-day strength test scheme combination is AND A1B3C2, that is, fly ash: fluorogypsum: calcium carbide slag = 50:30:20, and the optimal 7-day strength test scheme combination is A1B2C1, that is, fly ash: fluorogypsum: calcium carbide slag = 50:25:15. The optimal 28 day strength test scheme combination is A3B3C1, that is, fly ash: fluorogypsum: calcium carbide slag = 60:30:15.

4. RESULTS AND DISCUSSION

4.1. Phase Composition Analysis

The raw materials were prepared according to the optimal strength ratio, and the fragments in the center of the broken sample after the experiment were tested by X-ray diffraction on the samples of different ages, and the XRD of the fly-ash-fluoropygaster-calcium carbide slag gelling system at different ages was obtained, as shown in Figure 4.

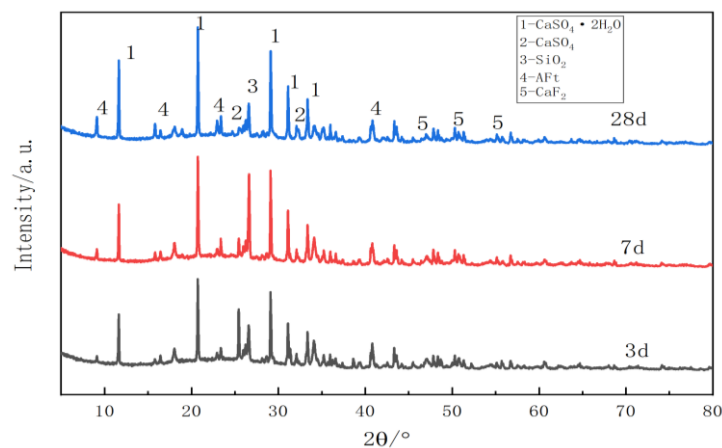


Figure 4. xrd

As can be seen from Fig. 4, the diffraction peak intensity of anhydrous gypsum is relatively high during the 3-day hydration reaction, while that of dihydrous gypsum is relatively weak, and a large amount of quartz is still unreacted. It can be seen from the 3-day and 28-day hydration that the diffraction peak of anhydrous gypsum gradually weakens, that of dihydrous gypsum increases, and that of ettringite also increases with the hydration reaction. The diffraction peak of quartz is decreased, which may form c-s-h gel with calcium carbide slag fly ash. In addition, it can be seen that calcium fluoride is generated by the reaction of calcium carbide slag with fluorogypsum, so the addition of calcium carbide slag plays a significant role in the fixation of fluoride ions.

4.2. Micromorphology Analysis

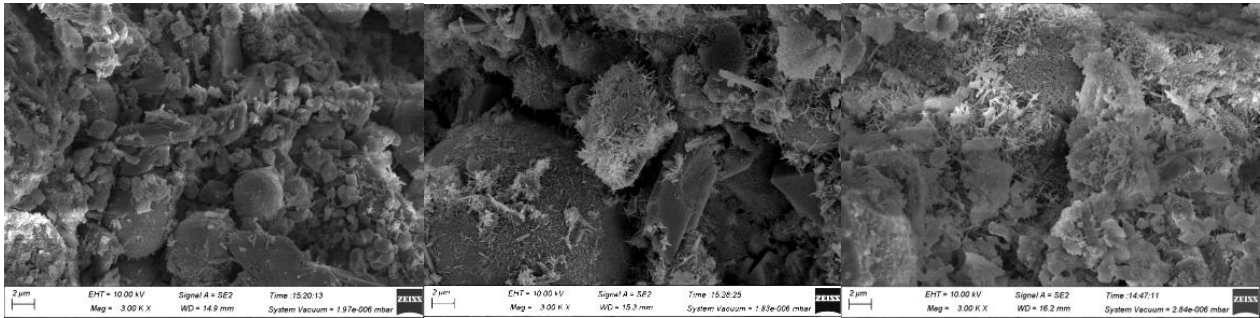


Figure 5. SEM diagram (a left picture: 3d; b middle picture: 7d; c Right picture: 28d)

It can be seen from Figure 5a that when hydration reaction is carried out to the third day, A large number of unreacted massive anhydrous gypsum and part of unreacted fly ash particles can be observed in the figure, accompanied by a small amount of plate-dihydrate gypsum and a trace of rod-shaped ettringite are formed. In the early stage, C-(A)-S-H gel is mainly filled in the needle-shaped crevasses of ettringite, indicating that the hydration reaction degree of the system is low. Therefore, the early strength of the sample is low. It can be seen from FIG. 5b that on the 7th day of hydration reaction, it can be observed that the quantity of anhydrous gypsum decreases significantly and a large amount of dihydrous gypsum is formed; meanwhile, the quantity, diameter and length of ettringite all increase and the bonding is extremely tight; the increase in the amount of C-S-H gel and ettringite co-encase the dihydrous gypsum, which makes the material more dense, indicating that the hydration reaction degree is further deepened at this time. Therefore, the strength of the sample increased in the middle stage. As can be seen from Fig. 5c, when the hydration reaction was carried out on the 28th day, the existence of fly ash particles was almost invisible, but a small amount of columnar dihydrate gypsum existed, and hydration products such as ettringite and csh gel were abundant and tightly combined, filling the pores and cracks. At the same time, a small amount of calcium fluoride was found on the surface of dihydrate gypsum. At this time, the overall hydration reaction degree is higher, and the strength is further improved.

4.3. Hydration Mechanism

Combined with the above SEM and XRD analysis, the hydration mechanism of the composite gelling system of fly ash, fluorogypsum and calcium carbide slag can be inferred as follows. After contact with water, fly ash, fluorogypsum and calcium carbide slag ionize Ca^{2+} , SO_4^{2-} , OH^- , F^- . The silica-aluminum glass in fly ash does not polymerize under the action of OH^- , Si-O-AL-O bond is broken, active silica-aluminum is dissolved, and C-S-H gel is formed by reaction with Ca^{2+} , SO_4^{2-} , OH^- , F^- in the system. Ettringite and insoluble calcium fluoride, SO_4^{2-} displace the coated SiO_4 in C-S-H gel, and continue to react with Ca^{2+} outside the coating layer to continuously generate C-S-H gel. The hydration reaction basically ends, and ettringite and gel are closely bonded to form a dense structure, and further improve the strength of the gelled material system.

5. CONCLUSION

(1) Using fly ash, fluoropygite and calcium carbide slag as raw materials to prepare composite cementation materials, through single-factor experimental analysis, fly ash in 50%-60%, fluoropygite in 20%-30%, calcium carbide slag in 15%-20% of the highest strength.

(2) Orthogonal experiments were carried out on the gelling system of fly ash, fluoropygite and calcium carbide slag according to single factor experiment. Through orthogonal experiments, the test scheme combination with optimal ratio of 3 d and optimal strength was determined as and A1B3C2, that is, fly ash: fluoropygite: calcium carbide slag = 50:30: The optimal test scheme combination for 20,7 days is A1B2C1, that is, fly ash: fluoropygypsum: calcium carbide slag = 50:25:15; The optimal 28 day strength test scheme combination is A3B3C1, that is, fly ash: fluoropygypsum: calcium carbide slag = 60:30:15.

(3) Through XRD, SEM and other test methods, the hydration mechanism of the composite gelling system of fly ash, fluoropygypsum and calcium carbide slag was explored. The results show that: In the early stage, the hydration products of the system were mainly C-(A)-S-H gel and ettringite. With the extension of curing period, the hydration reaction was further deepened, the number of hydration products increased, the porosity of the composite cementing material decreased, and the strength also increased. Among them, the reaction of calcium carbide slag and water-soluble fluorine in fluoropogon produced insoluble calcium fluoride, which had a certain effect on the curing of fluoride ions.

REFERENCES

- [1] Ma Zhengxian et al., preparing special masonry materials by using modified fluoropygypsum. *Comprehensive Utilization of mineral resources*, 2016(06): 55-60.
- [2] Jiang Chunzhi and Dong Fengzhi, *Comprehensive utilization and research progress of industrial by-product gypsum*. Shandong Chemical Industry, 2016. 45(09): pp. 42-44+47.
- [3] Ji LuoJun and Zhao Honglin, resource utilization of industrial by-product gypsum from the perspective of circular economy. *Sulfuric Acid Industry*, 2021(09): pp. 1-8.
- [4] Xie Jianhai et al., Study on properties of fluoropygypsum composite cementitious materials. *Bulletin of Silicate*, 2013. 32(04): pp. 772-775.
- [5] Li Jingke et al. Study on comprehensive utilization of industrial waste fluoropygypsum. *Gansu Metallurgy*, 2010. 32(03): pp. 105-109.
- [6] Qi Xianxiang, Performance analysis of fluoropygypsum as cement retarder. *Cement*, 2020(01): pp. 24-26.
- [7] Lv Yongliang, Zhang Siqiang and Zhao Hui, Practice of industrial fluoropygypsum as retarder in cement production. *Cement Engineering*, 2017(03): pp. 64-65+67.
- [8] Xie Longgui et al. Research progress of carbon sequestration technology for gypsum industrial waste. *Phosphorus and compound fertilizers*, 2022. 37(01): 32-35.
- [9] Liu Quan et al., Experimental research and development of fluoropygypsum based filling cementing materials. *Mining Research and Development*, 2019. 39(01): 36-39.
- [10] Wang, Y., et al., Effects of Aluminum Sulfate and Quicklime/Fluoropygypsum Ratio on the Properties of Calcium Sulfoaluminate (CSA) Cement-Based Double Liquid Grouting Materials. *Materials*, 2019. 12(8): p. 1222- 1222.
- [11] Bigdeli, Y., et al., Development of new pH-adjusted fluoropygypsum-cement-fly ash blends: Preliminary investigation of strength and durability properties. *Construction and Building Materials*, 2018. 182: p. 646-656.
- [12] Kuz, et al., Production of Portland cement using fluorine gypsum – hydrofluoric acid waste. *Magazine of Civil Engineering*, 2022. None(111): p. 11113-11113.
- [13] Qin Haizhong and Li Jia, Experimental study on the ratio of new paste filling materials based on fluorine gypsum. *Nonferrous Metals Engineering*, 2022. 12(09): 144-153.
- [14] Yao Yan, et al., Modification of waste fluoropygypsum and its applications as a cement retarder. *Journal of Central South University of Technology*, 2011. 18(05): p. 1402-1407.