Available online www.jsaer.com

Journal of Scientific and Engineering Research, 2021, 8(10):18-22

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Reasonable Content of Alkali Activator for Slag Titanium Gypsum Cementitious Material Based on Compressive Strength

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Abstract In order to obtain the reasonable dosage of activator for titanium gypsum cementitious material, the titanium gypsum and slag are mixed at 40:60, and three kinds of activators, water glass, sodium hydroxide and alum were used for composite admixture according to the proportion. A three-factor three-level orthogonal experiment was designed, the prism specimens were prepared and cured in the water tank for 3d, 7d, 28d, and the compressive strength indexes were tested respectively. The results show that the 3d, 7d, 28d compressive strength of the cementitious material increases with age. If the appropriate amount of composite activator is selected, its strength can reach the strength index of 32.5# slag Portland cement, of which the best dosage of activator is 1.5%Na_2SiO_3, 0.5%NaOH, 0.6%$KAl(SO_4)_2$.

Keywords Titanium gypsum; Slag; Cementitious materials; Compound activator; Compressive strength

1. Introduction

Alkali-activated cementitious materials use industrial solid waste as raw materials. Compared with the "two mills and one burning" in the process of preparing ordinary Portland cement, the raw material processing methods of alkali-activated cementitious materials are simple, and the preparation process has low energy consumption, low emissions, low-cost characteristics. To a certain extent, it has become one of the green and environmentally friendly gelling alternative materials. In recent years, the combination of titanium gypsum, fly ash, slag and other materials can effectively improve the physical properties of composite cementitious materials through the excitation of suitable activators.

Huisheng Shi et al. [1] studied a series of mechanical properties and durability of composite cementitious materials of titanium gypsum and fly ash, such as the strength, free linear expansion, and so on. The test results show that the reasonable combination of high-calcium fly ash and ordinary intact low-calcium fly ash combined with titanium gypsum has higher strength and elastic modulus, as well as suitable expansion rate and excellent durability. Zhendong Liu et al. [2] used titanium gypsum, cement and superplasticizer as raw materials to prepare cementitious materials. When 10% titanium gypsum and 1.2% CJ-1 superplasticizer are added, the flexural and compressive strength of cement mortar meet the strength index requirements of P.042.5 cement, and its setting time and stability are also qualified. Qiao D et al. [3] used 15% phosphogypsum, 38% fly ash and 17% acetylene sludge to prepare cementitious materials. They found no negative effects in rural road construction and could meet the road requirements. Deqiang Zhao et al. [4] uses 40% clinker, 35% fly ash, 15% phosphogypsum, and 10% steel slag to prepare the cementitious material for pavement base course. The compressive strength is 20%~50% higher than that of lime and fly ash stabilized gravel.

To sum up, in the application of road engineering, there are few researches on the road use of titanium gypsum, and most of them focus on the use of low-volume modified materials, and most of them require high-temperature treatment. This research intends to modify the new composite cementing material made by mixing titanium gypsum and slag in a certain proportion by adding a composite activator, in order to obtain better strength performance to meet the needs of road.

2. Materials and Test

2.1 Materials

Titanium gypsum is taken from a titanium gypsum accumulation site of Shandong Dongjia Group. Its main component is $CaSO_4 \cdot 2H_2O$. It is ground by a ball mill and passed through a 0.075mm sieve. The chemical composition is shown in Table 1.

Slag was purchased from Hebei Lingshou County Fuheng Mineral Trading Co., Ltd., and its chemical composition is shown in Table 1.

Water glass was purchased from Tianjin Damao Chemical Reagent Factory. Molecular formula: $Na_2SiO_3 \cdot 5H_2O$, molecular weight is 212.22, and Na_2O content is 28.2%~30.0%.

Sodium hydroxide was purchased from Yantai Shuangshuang Chemical Co., Ltd. Molecular formula: NaOH, molecular weight 40.00, NaOH content not less than 96.0%.

Alum was purchased from Tianjin Damao Chemical Reagent Factory. Molecular formula: $KAl(SO_4)_2 \cdot 12H_2O$, molecular weight 474.38,:$KAl(SO_4)_2 \cdot 12H_2O$ content is not less than 99.5%.

Table 1: Chemical composition of titanium gypsum (%)

Element	**CaO**	**Al_2O_3**	**SiO_2**	**MgO**	**Fe_2O_3**	**TiO_2**
Titanium gypsum	35.6	1.06	1.47	1.38	9.03	0.92
Slag	42.8	14.2	27.8	8.06	0.38	1.28
Element	**SO_3**	**MnO**	**Na_2O**	**Ignition loss**	**45μm sieve residue**	**80μm sieve residue**
Titanium gypsum	39.1	0.32	0.17	6.62	93.2	16.9
Slag	2.42	0.46	0.56	1.12	11.6	4.6

2.2 Test Method

The mortar strength test piece of the composite cementitious material is molded in accordance with "*T0506-2005 Cement Mortar Strength Test Method (ISO)*", then cured in a standard curing box for 24 hours and then demolded. Then it is cured in a water tank with a water temperature of 20±1℃ until the age to be tested. Take it out of the water 15 minutes before the test (breaking type), wipe off the surface deposits on the test piece, wipe off the surface deposits on the test piece, and cover it with a damp cloth, and finally measure its strength index. Orthogonal test method was used to study the reasonable dosage of composite activator in the titanium gypsum-based composite cementing material.

Table 2: Factors-Level table

Level	**Na_2SiO_3**	**NaOH**	**$KAl(SO_4)_2$**
1	0.5	0.3	0.6
2	1.0	0.5	0.8
3	1.5	0.7	1.0

Table 3: Test plan table

Sample	**Na_2SiO_3**	**NaOH**	**$KAl(SO_4)_2$**
1	0.5	0.3	0.6
2	0.5	0.5	1.0
3	0.5	0.7	0.8

4	1.0	0.3	1.0
5	1.0	0.5	0.8
6	1.0	0.7	0.6
7	1.5	0.3	0.8
8	1.5	0.5	0.6
9	1.5	0.7	1.0

3. Test Results and Discussion

3.1. Analysis of the Strength of Composite Cementitious Materials

Table 4 shows the strength of titanium gypsum-based composite cementitious materials with different content of composite activator.

Table 4: Compressive strength of test piece (MPa)

Sample	3d	7d	28d
1	0.5	0.3	0.6
2	0.5	0.5	1.0
3	0.5	0.7	0.8
4※	1.0	0.3	1.0
5	1.0	0.5	0.8
6	1.0	0.7	0.6
7	1.5	0.3	0.8
8	1.5	0.5	0.6
9	1.5	0.7	1.0

(※Sample 4 could not be molded in 3d, and disintegrated in water after being demolded in 7d.)

It can be seen from Table 4:

- The compressive strength increases with age.
- The 3d and 7d compressive strengths are the highest in Sample 3, with strengths of 20.92MPa and 26.30MPa respectively; the 3d and 7d compressive strengths are the lowest in Group 1 (12.06MPa) and in Group 7 (19.73MPa) respectively; The 28d compressive strength is the highest in Group 8 (35.87MPa), and the lowest in Group 2 (23.50MPa).
- From 3d to 7d, the compressive strength growth rate was the fastest in Group 1 (68.8%), and the lowest in Group 3 (25.7%); from 7d to 28d, the compressive strength growth rate was the fastest in Group 8 (81.8%).,and the lowest in Group 2 (3.0%).
- In the 28d compressive strength, Group 3, Group 5, Group 6, Group 7 and Group 8 can reach the strength index of 32.5# slag Portland cement.

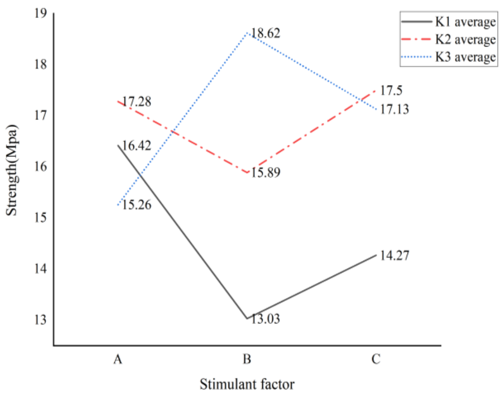

Figure 1: The average K value of 3d compressive strength

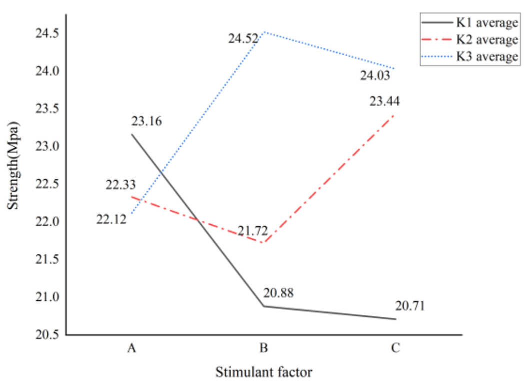

Figure 2: The average K value of 7d compressive strength

Figure. 1-4 can be obtained through data analysis. It can be seen that:

- NaOH has a greater impact on the 3d and 7d compressive strength of the composite cementitious material; it has a small impact on the 28d compressive strength.
- Na_2SiO_3 and $KAl(SO_4)_2$ have significant effects on the 28d compressive strength of composite cementitious materials.
- Within the scope of the study, the mortar strength of composite cementitious materials is positively correlated with the content of NaOH and Na_2SiO_3, and negatively correlated with the content of $KAl(SO_4)_2$.

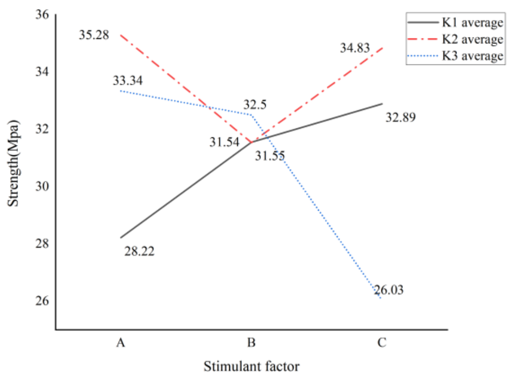

Figure 3: The average K value of 28d compressive strength

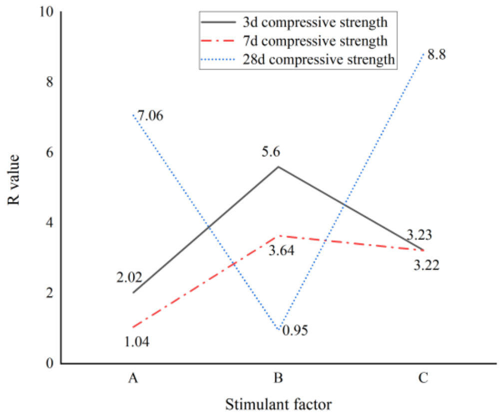

Figure 4: The R value of Compressive strength

3.2 Discussion

3.2.1 The Mechanism of Strength Growth

With the increase of the curing age, the slag plays a dual role in SO_4^{2-} and OH^-, and the volcanic ash effect is gradually exerted. The Al-O bond and the Si-O bond are broken, forming $AlO^{2-}$and SiO_3^{2-}, as shown in formulas 3.1 and 3.2; and AlO^{2-} and SO_4^{2-} further react to form AFt (ettringite), as shown in formulas 3.3 [5], which significantly increases the strength of the cementitious material.

$$SiO_2+2OH^- \rightarrow SiO3^{2-}+H_2O \quad (3.1)$$

$$Al_2O_3 + 2OH^- \rightarrow 2AlO^{2-}+H_2O \quad (3.2)$$

$$Ca^{2+} + AlO^{2-}+ OH^- + 2SO_4^{2-} \rightarrow AFt \quad (3.3)$$

Gypsum generates a certain amount of SO_4^{2-}, which makes Ca^{2+} react with the fractured Si-O to form hydrated calcium silicate gel (C-S-H) [6], as shown in formulas 3.4. The $Ca(OH)_2$ gel and The $Fe(OH)_3$ gel formed by the hydration of Fe^{3+} in titanium gypsum, tricalcium aluminate (C_3A) and tricalcium silicate (C_3S) in slag, promotes the hydration of C_3S and C_3A, and promote the formation of more C-S-H [7]. In addition, the free $[H_3SiO_4]^-$ in the gelling system can further react with AlO^{2-} to form hydrated calcium aluminosilicate gel(C-A-S-H) [8], as shown in formula 3.5, which works together with C-S-H to fill the gaps and improve strength.

$$Ca^{2+} + SiO3^{2-}+H_2O \rightarrow C\text{-}S\text{-}H \quad (3.4)$$

$$[H_3SiO_4]^-+AlO^{2-}+OH^-+H_2O + Ca^{2+} \rightarrow C\text{-}A\text{-}S\text{-}H \quad (3.5)$$

3.2.2 The mechanism of specimen disintegration

The hydration rate does not match the diffusion rate [9]. The formation of the system structure is affected by both the rate of formation of hydrates and the rate of diffusion into the system. If the rate of formation of hydrates is too fast, it is too late to diffuse into the surrounding space. Due to the unreasonable structural network produced by rapid hydration, there are many weak link, coupled with the heat generated by cement hydration is released at a high rate, cement stone is a poor conductor of heat, so the resulting thermal stress causes the weak link of the cement stone to form many micro-cracks. As hydration progresses, a large amount of AFt is formed. The AFt generated at this time in a limited space and has a great expansion potential to further expand the original micro-cracks or generate new cracks, and the cement stone structure becomes less dense, which affects the formation of strength. In this test, due to the relatively fast hydration rate of the composite cementitious material in the trial mold, such as tricalcium aluminate (C_3A) and tricalcium silicate (C_3S), a large amount of ettringite was produced in a short time, resulting in volume expansion and looseness, the strength cannot be formed, so the specimen cannot be molded in 3d. As the hydration rate decreases, the system 7d can develop a certain strength. Standard curing after demolding, the hydration speed becomes faster again in the sink, and the hydration products accumulate locally again. Because there is no restriction of the test mold, the test piece cracks from the inside to the outside, and the cracks gradually expand as the hydration progresses until the test Pieces disintegrated.

4. Conclusion

- The 3d, 7d, 28d compressive strength of the cementitious material increases with age, and the 28d compressive strength can reach 35.87MPa;
- NaOH has a greater impact on the 3d and 7d compressive strength of the composite cementitious material; Na_2SiO_3 and $KAl(SO_4)_2$ has a significant impact on the 28d compressive strength of the composite cementitious material;
- The strength of the slag-titanium-gypsum cementitious material can reach the strength index of 32.5# slag Portland cement with a suitable amount of composite activator;
- Within the scope of the study, the optimal dosage of the composite activator is 1.5% Na_2SiO_3, 0.5% NaOH, 0.6% $KAl(SO_4)_2$.

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