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Analysis of Active Mechanism of Chemical Activated Strontium Slag

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Abstract: In order to improve the activity of strontium slag, the mixed cementitious material of strontium slag cement was prepared by adding 30% (mass fraction) of pulverized strontium slag into cement. Chemical activators such as Na_2SiO_4, NaOH, $CaCl_2$, NaCl, $Ca(OH)_2$, Na_2SO_4 were added to the cementitious material. The flexural and compressive strength values of 3d, 7d, 28d were obtained by mortar strength test, and were used as the base with standard samples. The mechanism of activator improving the activity of strontium slag is analyzed. $CaCl_2$ and NaCl are cement early strength agents. So the substitution of strontium slag with silica powder is compared. The strength of strontium slag is judged by principle analysis. The results show that NaOH and Ca $(OH)_2$ are beneficial to the activation of SiO_2 and Al_2O_3, but the amount of ettringite is large and the strength is reduced, so there is a certain active excitation for strontium slag, but the effect is not very good; the addition of Na_2SiO_4 causes damage to volume stability and it is the worst of all activators. the compressive strength increases rapidly in 3d and 7d after adding NaCl, so it is mainly to stimulate the early strength of cement; The 28d compressive strength of strontium slag cement containing $CaCl_2$ is higher than that of strontium slag cement containing other chemical activators, which can reach 91% of the compressive strength of cement mortar. It is preliminarily judged that $CaCl_2$ has an exciting effect on strontium slag and the exciting effect is obvious.

Keywords: Pulverized Strontium Slag, Chemical Activation, Activity, Mechanism

1. Introduction

Currently, strontium slag is the most widely used strontium compound, which is widely used in color picture tubes, displays, electronic ceramics, industrial monitors, magnetic materials, military industry, medicine and other fields. For every 100,000 tons of strontium slag produced, about 800,000 tons of strontium salt waste residue (referred to as strontium residue) will be produced [1-3]. The research on the activity and utilization of strontium slag is still in its infancy. In China, strontium slag has not be listed as the type of industrial waste that can be used. The accumulation of strontium slag occupies land and pollutes the environment. According to incomplete statistics, at present, the total amount of strontium slag abandoned in the slag field has been up to about 40 million tons [4-5], and the road utilization value of strontium slag has been excavated, so that the environmental pollution has been improved, the cost of rural roads has been reduced, and the investment has been saved. A strontium slag cement concrete pavement test road has been built in rural areas of Chongqing city, China. Through the long-term performance observation of the test road, strontium slag cement concrete pavement can be widely used in low traffic volume roads [6]. Tang Boming applied strontium slag powder as Portland cement admixture The addition of strontium slag into cement has a certain active effect on the strength of cement [7]. Zhu Hongzhou made a series of research on strontium slag to analyze the feasibility of strontium slag as fine aggregate of cement mortar, the influence factors of mechanical properties of cement mortar with ground strontium slag, the design and

performance evaluation of lime strontium slag macadam base mixture and the road performance of strontium slag [8-11]. Si Chenhao has analyzed the leaching characteristics of strontium slag and applied it to the treatment of mine acid wastewater [12]. The content of strontium slag in the range of 20%-30% is expected to have a comprehensive strength effect on the early and late strength [13]. In this paper, the content of 30%(mass fraction) is used. Activity is the main reason that the utilization of strontium slag is limited. Tian Wenyu et al analyzed the influence of over-curing conditions and calcination temperature on the activity of strontium slag [14-15]. Currently, there is no study on the mechanism of improving the activity of strontium salt slag by chemical excitation. In this paper, chemical excitation of strontium slag cement mixed cementitious materials is carried out by adding chemical activators such as alkali and salt. The mechanism of improving the activity of strontium slag by activator is analyzed, which provides reference for engineering application.

2. Test Materials and Methods

2.1. Test Materials

Strontium slag: alkaline water quenching slag from the Red Butterfly Carbonate Strontium Plant in Dazu County, Chongqing city. The main physical properties of strontium slag are measured. The true density is 2.76g/cm^3, the natural packing density is 1.16g/cm^3, and the ignition loss is 6.8%.

White carbon black powder: white carbon black powder produced by Changzhou Jia Ye Chemical Co, Ltd., the natural packing density of white carbon black is 0.226g/ml^3.

Chemical reagents: sodium silicate (Na_2SiO_4), sodium hydroxide (NaOH), calcium chloride ($CaCl_2$), sodium chloride (NaCl), calcium hydroxide $(CaOH)_2$, sodium sulfate (Na_2SO_4) are all chemically pure.

Cement: P.O32.5, the main technical properties are shown in table 1.

Table 1. *Main performance indexes of cement.*

strength/MPa		setting time /min		Stability
3d	28d	Initial setting	Final setting	
21.96	40.4	183	418	qualified

2.2. Mix Ratio

The mix ratio of cement and strontium slag mortar mixed with different chemical activators is shown in Table 2. Standard sample P.O is used as reference comparison.

Table 2. *Mixing ratio of chemical additive strontium slag cement sand.*

Test number	admixture /g	Standard sand /g	cement /g	water /ml	strontium slag /g
P.O	-	1350	450	225	-
A	Na_2SiO_4	1350	315	225	135
B	$Ca(OH)_2$	1350	315	225	135
C	NaOH	1350	315	225	135
D	$CaCl_2$	1350	315	225	135
E	Na_2SO_4	1350	315	225	135
F	NaCl	1350	315	225	135

2.3. Evaluation Method of Activity of Strontium Slag

The activity of strontium slag was evaluated by mortar strength test method. The ground strontium slag was used to replace part of cement in the preparation of strontium slag cement mixed cementitious materials. The strength of the mixed cementitious materials mixed with different chemical activators was compared with the strength of the base cement mortar to reflect the activity of strontium slag.

3. Test Results and Analysis

Different chemical activator strontium slag mortar materials were obtained by mixing 30% (mass fraction) ground strontium slag into cement. According to the method of cement mortar strength test (ISO), 40 mm *40 mm *160 mm strontium slag mortar specimens were prepared. After 24 hours, the die was removed and maintained in water at (20+1) degrees Celsius until the prescribed age. The bending and compressive strength of the specimens were tested for 3, 7 and 28 days. The experimental results are shown in "Figure 1, Figure 2 and Figure 3".

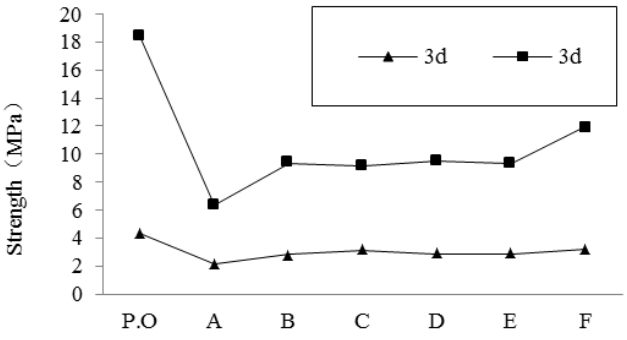

Figure 1. *Chemical activator 3d strength of strontium slag sand.*

From "Figure 1", it is shown that the compressive and flexural strength of 3d is the best when NaCl is added, and the compressive strength ratio is about 15% higher than that of other activators. NaCl and NaOH as activators had the highest flexural strength ratio for 3 days, reaching 73% of the standard sample. Na_2SiO_4 had the worst effect, and the other four had basically the same effect.

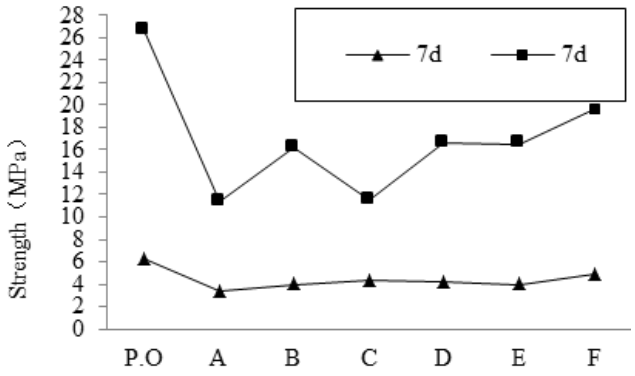

Figure 2. *Chemical activator 7d strength of strontium slag sand.*

From "Figure 2", it can be seen that the comprehensive and flexural strength of 7d can be the best when the Nacl is added, the compressive strength reaches 74% of the standard sample, which is basically the same as compressive strength ratio of 3d, the compressive strength of $Ca(OH)_2$, $CaCl_2$ and Na_2SO_4 reaches 62% of that of cement, and the flexural strength values of several activators are similar. The effect of NaOH and Na_2SiO_4 is not good.

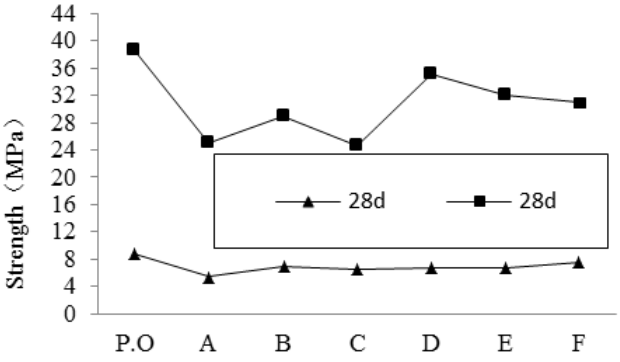

Figure 3. *Chemical activator 28d strength of strontium slag sand.*

From "Figure 3", it can be seen that the compressive and flexural strength of 28d is the best, adding $CaCl_2$ can reach 91% of the standard sample, which is the best excitation effect. Secondly, the compressive strength of Na_2SO_4 and NaCl reaches more than 80% of the standard sample, and the excitation effect is also very good. The effect of NaOH and Na_2SiO_4 is still the worst, and the compressive strength is 64% of the standard sample, which is 16% lower than other chemical activators.

The strength ratio of Strontium slag with NaCl in the early 3d and 7d can be increased by 10%-20% compared with that of unmixed Strontium slag. The early strength of $CaCl_2$ is lower than NaCl, but the strength of $CaCl_2$ in the 28d reaches more than 90% of the strength of cement mortar. However, NaCl, $CaCl_2$ and Na_2SO_4 are all early strength agents of cement, which may play an exciting role in the early strength of cement in varying degrees. In this paper, white carbon black is used to replace strontium slag in equal volume to see whether the early strength agent of cement can really stimulate the strength of strontium slag.

Taking 27g white carbon black powder as volume to replace 135g strontium slag, white carbon black powder absorbs water relatively, so the working performance of the specimens is not good while keeping 225ml water unchanged, and the stirring is very dry and thick. The experimental results are shown in "Figure 4, Figure 5 and Figure 6."

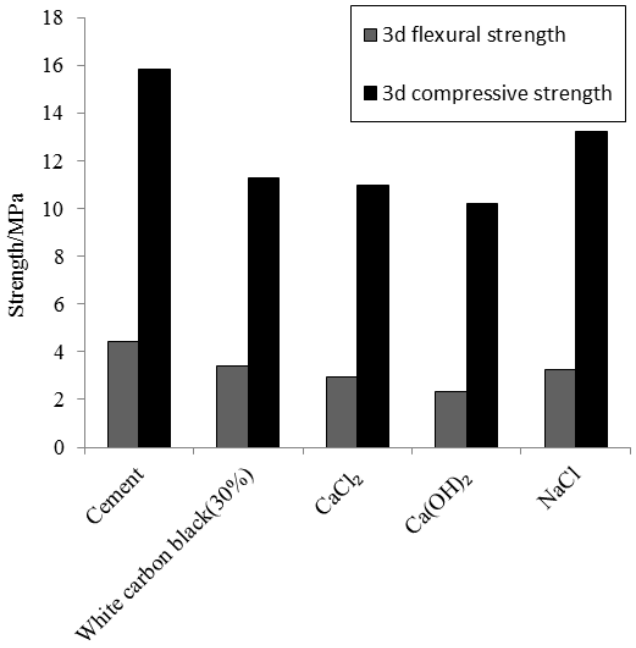

Figure 4. *Chemical activator 3d strength of white carbon black cement.*

From "Figure 4", it can be seen that the flexural strength of cement paste can reach 77% after adding 30% white carbon black for 3 days, 74% when adding NaCl, 67% when adding $CaCl_2$, and the flexural strength declined by up to 20% when adding $Ca(OH)_2$. The compressive strength of cement mortar with 30% white carbon black in 3d accounts for 71% of the strength of cement mortar. The compressive strength of cement mortar with NaCl can reach 83%, while $CaCl_2$ and $Ca(OH)_2$ decrease slightly.

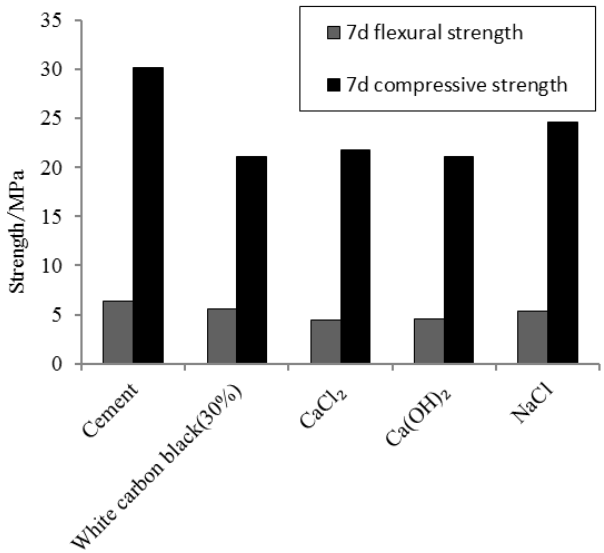

Figure 5. *Chemical activator 7d strength of white carbon black cement.*

"Figure 5" shows that the flexural strength of cement paste can reach 88% after adding 30% white carbon black for 7 days, 85% when adding NaCl, and 17% when adding $CaCl_2$ and $Ca(OH)_2$. The 7d compressive strength of cement paste with 30% white carbon black accounted for 70% of the strength of cement paste. The compressive strength ratio of cement paste with $CaCl_2$ and Ca $(OH)_2$ changed little, and the compressive strength ratio of cement paste with NaCl could reach 82%.

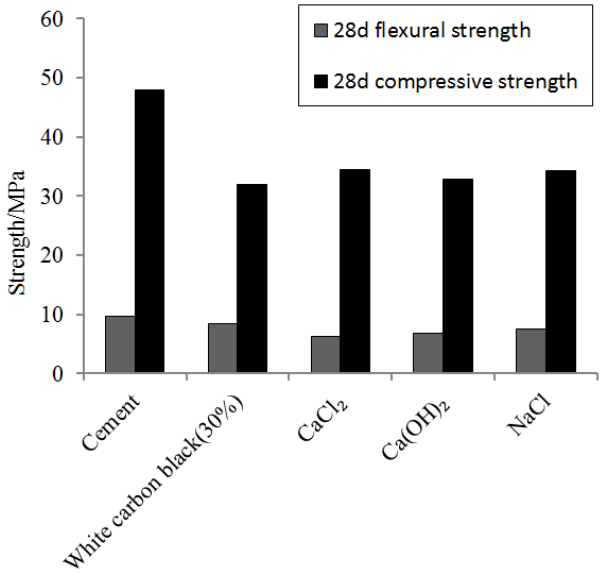

Figure 6. *Chemical activator 28d strength of white carbon black cement.*

From "Figure 6", it shows that the flexural strength of cement paste can reach 87% after adding 30% white carbon black powder for 28 days, 78% after adding NaCl, and the effect of adding $CaCl_2$ and $Ca(OH)_2$ is relatively poor. The 28 days compressive strength of cement paste with 30% white carbon black accounted for 67% of the strength of cement paste, the compressive strength ratio of cement paste with $Ca(OH)_2$ reached 69%, and that of NaCl reached 72%. Compared with the compressive strength of 3d and 7d, the compressive strength of cement paste with $CaCl_2$ increased by 72%.

From the analysis of test data, NaCl can stimulate the strength of cement, and it can also stimulate white carbon black cement. So NaCl should stimulate the early stage of cement in strontium slag cement. The strength ratio of $Ca(OH)_2$ in white carbon black powder is lower than that of white carbon black cement without chemical activator. From the data, it can be seen that $Ca(OH)_2$ has little stimulating effect on cement in the system of strontium slag cement and cementing, and its strength has slightly improved, which has certain stimulating effect. The strength ratio of white carbon black cement system with $CaCl_2$ is basically the same as that of white carbon black cement without $CaCl_2$, which indicates that $CaCl_2$ does not play an exciting role in white carbon black cement system. But in strontium slag cement, the 28 days strength ratio of the strontium slag cement with $CaCl_2$ is obviously higher than that of the reference mortar and can reach 91% of the compressive strength of the cement mortar. It is preliminary judged that calcium chloride has an exciting effect on the strontium slag, and the exciting effect is obvious.

4. Mechanism Analysis of Activator Improving the Activity of Strontium Slag

4.1. The Activation Principle of Alkali to Strontium Slag

According to the structural characteristics of strontium slag, it is thought that the strontium slag can be cementitious. First of all, there must be enough polar ions in aqueous solution, such as OH^-, and these polar ions are required to enter the holes in the vitreous structure through the "protective film" on the surface of strontium slag vitreous, and then to disperse and dissolve the strontium slag vitreous body by their interaction with the active cation Ca^{2+} and Sr^{2+}. Solution, and then in the solution we have to ensure that the newly formed hydration is a highly supersaturated solution, and can maintain enough time to achieve the nucleation and growth of hydration products, and then overlap each other to form a structural network.

On the other hand, from the chemical point of view, OH^- not only react with active cation, but also disperse and dissolve strontium slag vitreous. Moreover, it can form ions with the strontium slag vitreous network to form hydrated calcium silicate and calcium aluminate hydrate.

In this way, OH^- gradually hydrate strontium slag from outside to inside, and the strength of strontium slag is produced by C-S-H gel, ettringite and dihydrate gypsum. Unlike other pozzolanic materials, hydrated products contain more ettringite, which can form skeletons and increase the strength of the system in the early stage of production. However, too much production, especially at the later stage of hydration, will cause expansion, resulting in a slight crack in the system structure resulting in a decrease in strength. The formation and crystal structure of ettringite are related to the pH value of the system. The higher the pH value is, the higher the concentration of OH^- in the system is, the more the amount of ettringite is, and the needle-like crystals with aggregated morphology radiate outward, resulting in larger expansion value. When strong alkali NaOH is added into the system, on the one hand, it is favorable for the activation of active SiO_2 and active Al_2O_3; on the other hand, it greatly increases the alkalinity of the system, causes more ettringite formation and expansion, causes micro-cracks in the system and reduces the strength of the system. Frequently, the latter is in the upper hand, which makes the activation effect of NaOH on strontium slag not good.

4.2. Activation Mechanism of Salts on Strontium Slag

The addition of Na_2SiO_4 can provide a large amount of silicate ions for strontium slag cement, but the application of Na_2SiO_4 in the excitation of strontium slag cement mixtures has a poor effect. In addition, NaOH is produced by hydration reaction of Na^+ with water, and its excitation effect is also poor

as mentioned above. Na_2SiO_4 has the lowest strength ratio among all the activators.

The addition of Na_2SiO_4 to fly ash with high calcium usually has obvious activation effect, and it also plays a certain stimulating role in the application of strontium slag. The compressive and flexural strength ratio of the fly ash with Na_2SiO_4 is increased by 5%-10% compared with that of the fly ash without activator. The calcium content in strontium slag is less than 30%. Moreover, due to the production of raw materials and processes of strontium slag, there are more SO_3 in the strontium slag. Adding Na_2SO_4 will lead to excessive sulfur content and is easy to produce ettringite, which will destroy the volume stability.

Using $CaCl_2$ as an early strength agent for pozzolanic active material silicate products can improve the strength of products to varying degrees, but its action is not in the volcanic ash active material itself, but by accelerating the lime digestion and increasing the solubility of lime in water, thereby enhancing the OH^- concentration in the solution. At the same time, the formation process of sulphoaluminate is accelerated. In the presence of NaCl, the solubility of aluminate and gypsum increases. The calcium aluminate chloroaluminate formed is a kind of compound with poor stability. When gypsum exists, it can produce calcium sulphoaluminate and become a stable compound. The results show that there is a certain relationship between the content of active silicon aluminum and soluble silicon and aluminum content in pozzolanic active materials and the intensity of steam curing. In the silicate products with pozzolanic active materials, improving the content of soluble silicon and aluminum can accelerate the development of early strength of silicate products with pozzolanic active materials, and adding soluble silicon aluminum materials to improve the early strength of pozzolanic active materials in hydrothermal synthesis. Degree is due to the early hydration reaction. The first part of the reaction is the soluble silicon aluminum in pozzolanic active materials. However, the total soluble silicon and aluminum in pozzolanic active materials is only about 10%. When the soluble silicon aluminum is added, more hydrated calcium sulphoaluminate C-S-H gel can be formed at the early stage of hydration reaction, so that the early strength of the product is greatly increased, and the strength in the latter stage can be steadily increased.

5. Conclusion

The addition of NaOH and $Ca(OH)_2$ has both positive and negative effects on the strontium slag cement cementitious materials: on the one hand, it is beneficial to the activation of SiO_2 and Al_2O_3; on the other hand, it greatly increases the basicity, the quantity of ettringite formation and expansion, which causes micro-cracks and reduces the strength of the system. NaOH and $Ca(OH)_2$ have certain activation to strontium slag, but the effect is not good.

After joining Na_2SiO_4, strontium slag cement cementitious material will make the sulfur content exceed the standard, easy to produce ettringite, destroy the volume stability, and Na^+ react with water to form sodium hydroxide. Na_2SiO_4 is the worst in all activators.

After adding NaCl, the early compressive strength of cement strontium slag cementitious material increases rapidly in 3d and 7d. By adding white carbon black instead of strontium slag, the early strength of cement is mainly stimulated by adding NaCl as early strength agent.

For the use of chemical admixtures, the catalytic effect of activator on the formation of hydration products can improve the workability and strength of mortar. Among them, $CaCl_2$ has the best effect, and the 28 days compressive strength of cement mortar reaches 91%. By adding white carbon black instead of strontium slag, $CaCl_2$ has obvious stimulating effect on strontium slag.

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