Study on Phosphorus Slag Activation Technology and Preparation of Phosphate Slag-Based Cementitious Materials

Liping zhu*

College of Chemistry and environmental science, Qujing Normal University, Qujing 655011

*correspondence author: Liping zhu  E-mail: 254969980@qq.com

Abstract: In the paper, phosphorus slags were the main raw material. Orthogonal experiment method and single factor experiment method were used to determine the optimal process parameters for exciting phosphorus slag portland cement. The results show that the phosphorus slag mixture contained 0.05-0.07% triethanolamine, 1.5-2% NaCl, 1.5-1.8% Na₂SO₃. The phosphorus slag-based cementitious material was prepared by using the superior phosphorus slag active excitation scheme. The early and late activity indexes of the phosphorus slag-based can effectively support the large-scale resource utilization of phosphorus slag.

1. Introduction

It is commonly known that phosphorus slag is one of the most significant industrial solid wastes from the wet processes of yellow phosphorus production. Currently, over 35 million tons of phosphorous slag are produced annually in China (Wang et al., 2013). The cumulative amount of 50 million tons. At present except a few used in raw cement mixture (phosphorus slag utilization ratio of 60%), most is given priority to with the outdoor storage. Phosphorus slag is mainly composed of calcium oxide and silicon oxide, containing a small amount of phosphorus and fluorine[2]. Such a huge amount of phosphorus slag not only occupies the farmland, but also causes severe pollution to the surrounding environment due to some of its harmful components, such as soluble P₂O₅ and F. According to the composition of phosphorous slag[3], it’s resource-based utilization which is the main field of cement building materials industry[4]. However, the experiment has found that phosphorous slag as cement additive has some disadvantages such as low early strength, long setting time and low content, which limit its large-scale application[5]. Aiming at the problems existing in the application of phosphorous slag which in the field of cement and building materials, this paper studies the activation technology of phosphorous slag, and then prepares phosphorous slag-based cementitious materials[6], so as to provide technical support for the large-scale utilization of phosphorous slag which in the field of cement and building materials[7].

2. Material and Methods;

2.1 Experimental material
2.1.1 Principal raw material
The main components are shown in Table 1.

| Chemical composition of main raw materials/wt% | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O | SO₃ | other |
|-----------------------------------------------|------|-------|-------|------|------|------|------|-----|-------|
| Phosphorus slag                               | 42.3 | 4.03  | 0.67  | 42.4 | 1.67 | 0.62 | 0.39 | 2.32| 5.6   |
| Calcime                                       | 17.1 | 5.6   | 1.5   | 60.0 | 14.7 | /    | /    | /   | 1.10  |
| Quartz sand                                   | 99   | 0.22  | 0.015 | 0.023| 0.011| 0.06 | /    | /   | 0.67  |

(2) Chemical reagent
Analysis of pure sodium hydroxide, analysis of pure sodium carbonate, triethanolamine, analysis of pure sodium sulfite, analysis of pure sodium nitrite and other chemical activators, industrial water glass.

2.2 Experimental equipment and testing instruments
Laboratory equipment: jaw crusher (PE100X 60), cone ball mill (XMQ - 67G), electric drum wind drying oven (101-1A), planetary cement mortar mixer (JJ - 5), plastic sand vibration table, sanlian mould (40mm×40mm×160mm), atmospheric wet and heat curing box the highest temperature (97 ℃), Pressure maintenance boxes (pressure 0.8 MPa), scales, measuring cylinder, thermometer, etc.
Detection equipment: LS603 laser particle size meter, electro-hydraulic folding and compression resistance test machine, etc.

2.3 Experimental method and process route
The raw material is phosphorous slag, taking compressive strength and flexural strength of samples at different ages as evaluation indexes, the effects of mechanical activation, the chemical activation and composite activation on phosphorous slag activity were studied to obtain better process conditions for the preparation of phosphorous slag and cementitious materials.

Refer to GB/T1596-2005 for test of activity index of phosphorous slag. The calculation formula is shown in formula 1.

\[ H = \frac{R}{R'} \times 100\% \]

In the formula: H — Activity index, %; R — Compressive strength of phosphorous slag and colloidal sand samples for 28 days, MPa; R' — Compressive strength of standard colloidal sand sample at 28 days, MPa.

3. Results and Discussion;

3.1 Influence of mechanical activation on phosphorous slag activity
Only when the gelling material reaches a certain fineness can it have the gelling property, and only when the original phosphorous slag is modified by mechanical grinding can it have the gelling activity. The effect of different grinding time on the residue of phosphorous slag-325 mesh sieve was studied, and the results were shown in FIG.2. With the extension of grinding time, the residue of ~325 mesh screen gradually decreased. When the ball grinding time was 90min, the residue of ~325 mesh screen was 4%. When the grinding time was prolonged, the sieve residue did not significantly decrease, but slightly increased. Phosphorus slag is
mainly composed of silicon aluminate vitreous (80%~90%) and a small amount of crystalline phase, vitreous grinding easily broken, as the grinding time extended, sieve allowance rapidly decreases, and when the grinding time is greater than 90 min, fine particles is more, the material of the specific surface area and surface energy increase sharply, reunion between particles, a "broken — reunion reunited — secondary crushing" the process of dynamic balance, to achieve "grinding limit", continue to increase the grinding time is difficult to continue to reduce the sieve allowance, considering sieve allowance, grinding efficiency and energy consumption, the optimal grinding time of 90 min.

![Fig.2 Effect of grinding time on the ratio of sieve residue](image1)

![Fig.3 Effect of grinding time on activity index](image2)

The standard sample was prepared according to the JGT/t98-2010 masonry mortar mixture design regulations, and the effect of grinding time on the activity index (strength within 28 days) was investigated. The results are shown in figure 3. From 50 to 80 min, the activity of phosphorous slag increased with the prolonging of grinding time, and then decreased slightly.

3.2 influence of chemical activator on phosphorous slag activity
The standard sample was prepared according to JGT/T98-2010 masonry mortar mix design regulations. 1.3% chemical activator was added (calculated by the quality of phosphorous slag) to investigate the influence of phosphorous slag powder on the activity of phosphorous slag. The results are shown in table 2.

| Activator type | Phosphorus residue activity index/% |
|---------------|-----------------------------------|
| 0             | 47.39 54.08                       |
| Na₂SO₄        | 50.34 58.06                       |
| NaCl          | 61.9 69.01                        |
| K₂SO₄         | 50.78 54.95                       |
| CaCl₂         | 47.91 69.72                       |
| CaSO₄         | 47.8 54.69                        |
| Na₂SiO₃       | 53.56 60.12                       |
| Al₂(O₄)₃      | 52.45 66.22                       |
| Na₂SO₃        | 55.49 61.75                       |
| NaOH          | 50.56 58.67                       |
| (NH₄)₂SO₄     | 41.5 40.74                        |

As shown in table 1, trace amounts of NaCl, Na₂SiO₃, sodium sulfite, aluminum sulfate, NaNO₂ early and late activity of phosphorus slag were significantly improved, the trace of
Na$_2$SO$_4$, NaOH, K$_2$SO$_4$ early and late activity of phosphor slag, but of a smaller increase in trace amounts of CaSO$_4$ to not significantly affect the activity of the phosphorus slag, CaCl$_2$, early active effect of phosphorus slag is not obvious, but improve the activity of the late relatively obvious, (NH$_4$)$_2$SO$_4$ on the early and late activity of phosphor slag are adversely affected.

3.3 Better ratio of chemical activators

The standard sample was prepared according to JGT/T98-2010 masonry mortar mix design regulations. Triethanolamine, NaCl and Na$_2$SO$_3$ were added to investigate the effect of the mix ratio on the activity of phosphorous slag.

As shown in FIG. 4, as the proportion of triethanolamine increases, the activity index gradually increases. When the ratio is greater than 0.07%, the activity index no longer increases, and the optimal ratio is 0.05%-0.07%.

Based on the addition of 0.05% triethanolamine, the influence of NaCl and Na$_2$SO$_3$ on the activity of phosphate slag Portland cement and the optimal ratio were investigated. As shown in FIG. 5, NaCl significantly promoted the activity of phosphate slag Portland cement, and the compressive strength activity of 3d and 28d increased first and then stabilized with the increase of proportion.

The optimal plan to stimulate the activity of phosphate slag is to mix 0.05-0.07% triethanolamine, grind it for 80min, add 1.5-2% NaCl, 1.5-1.8% Na$_2$SO$_3$, and the early and late activity index of phosphate slag silicate cement (ratio of phosphorus slag to cement 1:1) can reach more than 80%. The use of 52.5 cement can reach the standard of 42.5 cement.

4. Conclusions

(1) Both mechanical activation and chemical activation can improve the activity of phosphorous slag, while mechanical activation or chemical activation alone is not ideal;
(2) The optimal plan to stimulate the activity of phosphorous slag was to mix 0.05-0.07% triethanolamine with phosphorous slag, grind it for 80min, and add 1.5-2% NaCl and 1.5-1.8% Na₂SO₃.

(3) The early and late activity index of phosphate slag Portland cement (the ratio of phosphate slag to cement 1:1) can reach more than 80% by using the better activation scheme of phosphate slag. The use of 52.5 cement can reach the standard of 42.5 cement, which can strongly support the large-scale resource utilization of phosphate slag.

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