Preparation and Performance Investigation of Optimized Cement-Based Sealing Materials Based on the Response Surface Methodology

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ABSTRACT: A new cement-based sealing material, which used Portland cement (PC) as a raw material and supplemented several gel components, such as accelerator, alkali activator, suspension agent, expansion agent, reinforcing agent, was prepared in this work. The effects of these components on the fluidity, setting time, and expansion rate of these sealing materials were investigated by an orthogonal test. The results show that the water−cement ratio and the reinforcing agent content, the accelerant content and the water−cement ratio, and the expansion agent content and the accelerant content are the most important influencing factors on fluidity, setting time, and expansion rate, respectively. In addition, the regression models and response surfaces of the factors were established using a multiple linear regression method. By this means, the influences of the two main factors on each performance of this sealing material were accurately and intuitively reflected for obtaining the optimal value in the optimization area. The results indicate that the sealing materials possess the best performances when the water−cement ratio is 1.1, the accelerant content is 50%, the expansion agent content is 0.1%, and the reinforcing agent content is 3%, which is corresponding to a fluidity of 360−380 mm, an initial (final) setting time of 60 (80)−80 (100) min, and an expansion rate of 2−12%. Furthermore, the microstructures of the optimized sealing material also reveal that the main hydration products of PC are transformed from layered Ca(OH)₂ crystals into fine needle-like AFt crystals and C–S–H gels by the promotion effect of the optimizing ratio, thus leading to a more compact structure of optimized cement-based sealing materials.

1. INTRODUCTION

Coalbed methane (CBM) is a kind of unconventional natural gas mainly adsorbed to coal seams and their surrounding rock.¹ As its pressure and concentration increase considerably, CBM has become one of the main hazards in coal mines.²⁻³ CBM extraction can not only reduce the risk of gas outburst but also yield clean energy and improve the efficiency of energy utilization.⁴⁻⁵ The average CBM extraction concentration in China is lower than 20 and 80% of the air entering the drainage system under a low negative pressure.⁶⁻⁷ There are two ways to increase the CBM extraction concentration: (1) to address problems, such as small pore size and massive adsorption in low-permeability coal seams, by means of hydraulic fracturing, hydraulic cutting, and coal seam water injection⁸⁻¹¹ and (2) to improve the sealing effect through narrowing down the gas leakage channels of boreholes.¹²⁻¹⁴ The former has been widely used, whereas the latter still has a long way to go with respect to the sealing material. Both sides of the roadway undergo yield deformation due to concentrated stress. Then, the concentrated stress is transferred into the coal seam to reach dynamic balance, thus forming a pressure relief area in the roadway.¹⁵,¹⁶ Zhang et al.¹⁷,¹⁸ simulated the failure process during coal seam roadway mining, analyzed the factors affecting gas leakage in the extraction process, and found the reasonable sealing depth and grouting parameters. According to the factors affecting gas leakage, Wang et al.¹⁹ proposed to inject different sealing materials into different stress areas to seal the gas leakage channels of the coal seam.

Since relatively perfect methods have been proposed to solve gas leakage in the pressure relief area, the fractured area of the borehole has become the main gas leakage channel currently. The optimal sealing material for this area features strong fluidity and microexpansion.²⁰,²¹ Therefore, cement-based sealing materials, which boast advantages of strong fluidity and high strength, have attracted the attention of researchers. However, ordinary cement materials tend to shrink after solidification. Considering this fact, a certain number of

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additives are added into the cement to improve its performance, enhancing the microexpansion rate of the sealing material during hydration, controlling the setting time, and increasing the fluidity and mechanical strength. Zhou et al.22,23 carried out single-factor experiments on cement-based sealing materials with different additives and water–cement ratios and determined the influence of each factor on the expansion performance of sealing materials by the response surface methodology (RSM). Lian et al.24-26 explored the fluidity and compressive strength of the fly ash grouting material and the new cement-based reinforcement material, respectively. Besides, by analyzing the influence of different water–cement ratios and additive contents on the material properties, they determined the optimal material ratio that can lead to a reasonable fluidity and compressive strength. Cui et al.27 mixed raw lime, binder, clay, and fly ash at different ratios to prepare slurries with different water–cement ratios and material ratios. Moreover, they modified the water–cement ratio and material ratio in the fluidity test based on the results of the expansion optimization test.

The single-factor experiment can only reveal the variation trends of the performances of sealing materials, yet it can hardly help analyze the effects of all material components on the performances. Su et al.28 studied the effects of various factors on the solidification time, solidification ratio, and water segregation rate of cement–clay slag composites via an orthogonal test and obtained the optimal ratio to achieve the best performance of the material. By adopting the orthogonal experimental design and multiple linear regression analysis, Hao et al.29-32 established the empirical relationship between the influencing factors (such as water–cement ratio and additive content) and the properties of the materials (such as fluidity, solidification time, compressive strength, and expansion rate). Besides, they obtained the optimal ratio of the materials and the significance level of the influencing factors. Yuan et al.33 deduced the polynomial regression model of cement–sodium silicate grouting by analyzing the experimental data, which provided guidance for optimizing its anti-washing performance. Tian et al.34 predicted and optimized the variables affecting the fluidity and mechanical strength of road-ground polymer grouting materials through the combination of RSM and multiobjective particle swarm optimization algorithm. The results indicated a strong interaction between water and NaOH. Mou et al.35 obtained the main influencing parameters and relationships of grouting by gray correlation and regression analysis. It was concluded that the fluid loss and water absorption of drilling are the main determinants of cement slurry volume. Sun et al.36 predicted the Young’s modulus of coal concrete with the aid of the optimized BPNN-BAS model and established a nonlinear relationship model of compressive strength to determine the correlation among the influencing factors. The above studies on the preparation and performance optimization of sealing materials employed laboratory tests to explore the variation trend of material performance and used statistical methods to establish models for optimizing the material ratio.

This study is aimed at improving the sealing quality of gas drainage boreholes. First, the performance indicators of new cement-based materials with different ratios were tested through an orthogonal test to determine the fluidity, setting time, and expansion rate of the sealing material under the optimal ratio. Meanwhile, the regression models of the performances of the new cement-based sealing material were established through multiple linear regression analysis. Moreover, the influences of material ratios on the performances of the sealing materials were intuitively reflected through the RSM, and then the optimal values of all components were selected in the optimization area. Furthermore, the microstructures of the optimized materials were analyzed with the aid of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The research results can be applied to engineering practice to improve the sealing effect of boreholes and the efficiency of gas drainage.

2. RAW MATERIALS AND METHODOLOGIES

2.1. Raw Materials. The raw materials used in this investigation include Portland cement (PC) and other additives, such as accelerator, alkali activator, suspension agent, expansion agent, and reinforcing agent. PC is produced in Qian-ye Co. Ltd, China, with CaSO₄·2H₂O as the alkali activator with a purity of 95%, Al powder as the expansion agent, and silica fume as the reinforcing agent. The chemical compositions of PC and some other additives are listed in Table 1, and Figure 1 shows the XRD patterns of the raw materials.

| Table 1. Chemical Compositions of the Materials (wt %) |
|---|---|---|---|---|---|---|
| material | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ |
| PC | 61.67 | 21.75 | 5.57 | 3.58 | 2.21 | 2.36 |
| accelerator | 46.12 | 9.98 | 28.86 | 2.63 | 0.56 | 11.85 |

Figure 1. XRD spectra of mineral compositions.

The mineral compositions of PC are mainly 3CaO·SiO₂ (C₃S), 2CaO·SiO₂ (C₂S), 3CaO·Al₂O₃ (C₃A), 4CaO·Al₂O₃·Fe₂O₃ (C₄AF), and some free calcium oxide and magnesite, while the accelerator mainly consists of 3CaO·Al₂O₃·CaSO₄ (C₃A·S). The hydration products of C₃S and C₂S minerals are C–S–H gels, C₃A and C₄AF are conducive to hydration to form CH gel. C₃A·S′ can quickly react with gypsum to form ettringite (AF₆) and aluminum hydroxide gel (AH) in the early stage of hydration, which can improve the formation state of the hydration products.

2.2. Orthogonal Test Design and Results. The orthogonal test is an experimental design method based on multiple factors and levels, which helps select representative design schemes from substantial test combinations. This method was used to optimize the ratios of the sealing materials in order to obtain sealing materials that meet the engineering requirements. The experimental program is based on a six-factor, five-level orthogonal experimental design, and the test factors and levels are listed as A₆B₃C₄D₅E₆F₇ in Table 2; A–F parameters represent the types of factors influencing the
Table 3. Orthogonal Test Design

| group number | factor | A (%) | B (%) | C (%) | D (%) | E (%) | F (%) |
|--------------|--------|-------|-------|-------|-------|-------|-------|
| 1            | (A₁)  | 0.9   | 25    | 3     | 1     | 0.1   | 1     |
| 2            | (B₁)  | 1.0   | 30    | 4     | 2     | 0.2   | 2     |
| 3            | (C₁)  | 1.1   | 40    | 5     | 3     | 0.3   | 3     |
| 4            | (D₁)  | 1.2   | 50    | 6     | 4     | 0.4   | 4     |
| 5            | (E₁)  | 1.3   | 60    | 7     | 5     | 0.5   | 5     |
| 6            | (F₁)  |       |       |       |       |       |       |
| 7            | (A₂)  | 0.9   | 25    | 3     | 1     | 0.1   | 1     |
| 8            | (B₂)  | 1.0   | 30    | 4     | 2     | 0.2   | 2     |
| 9            | (C₂)  | 1.1   | 40    | 5     | 3     | 0.3   | 3     |
| 10           | (D₂)  | 1.2   | 50    | 6     | 4     | 0.4   | 4     |
| 11           | (E₂)  | 1.3   | 60    | 7     | 5     | 0.5   | 5     |
| 12           | (F₂)  |       |       |       |       |       |       |

software of orthogonal test assistant. The parameter A represents the water–cement ratio, B represents the contents of the accelerator, C represents the contents of the alkali activator, D represents the contents of the suspension, E represents the contents of the expansion agent, and F represents the contents of the reinforcing agent. The content of the additives accounts for the total mass fractions of the sealing material. The aim was to analyze the function of each component and to optimize the fluidity, setting, and expansion performance of the sealing material.

2.3. Testing Methods. 2.3.1. Orthogonal Test. According to the Cement Mortar Fluidity Determination Method (GB/T2419-94), the fluidity of the slurry was tested by a truncated cone mold. The average of the maximum diameter and vertical diameter was taken after allowing the slurry to flow on a glass plate for 30 s. The measuring device is shown in Figure 2a. The initial and final setting times of the slurry were tested with the aid of a Vicat apparatus according to the Cement Standard Consistency Water Consumption, Setting Time, Stability Test Method (GB1346-89). After completing the slurry preparation for 30 min, the above indicators were measured every 5 min. The measuring device is shown in Figure 2b. The concretion of the sealing material was wrapped by the wax seal method. Afterward, the volume change of water (V) after expansion was observed by the drainage method to calculate the expansion rate of the material: R = (V₁ − V₀) × 100%/V₀. The measuring device is shown in Figure 2c.

2.3.2. Microstructure Analysis. The SEM (Quanta FEG 250 FE-SEM from FEI, USA) test was aimed at probing into the micromorphology of the hydration products with an accelerator voltage of 20 kV. The measuring device is shown in Figure 3a. The XRD (SmartLab XRD from Kubashiki Kaisha, Japan) test was used to explore the compositions of the hydration products with a scanning speed of 10°/min and a scanning angle of 5°–55°. The measuring device is shown in Figure 3b.

3. ORTHOGONAL TEST RESULTS AND ANALYSIS

3.1. Analysis on Factors Influencing Fluidity. Fluidity is an important indicator for sealing materials. The changes of fluidity in the orthogonal test are illustrated in Figure 4. The test results of each group were numbered according to different water–cement ratios as A₁–A₅. The value difference of maximum and minimum range analysis is denoted by R. The range of the maximum and minimum values of each group was analyzed to determine the most suitable ratio of water to cement.

Table 4. Orthogonal Test Results

| group number | fluidity (mm) | initial setting time (min) | final setting time (min) | expansion rate (%) |
|--------------|---------------|----------------------------|-------------------------|-------------------|
| 1            | 363           | 342                        | 25380                   | 3.13              |
| 2            | 388           | 308                        | 25380                   | 3.13              |
| 3            | 370           | 354                        | 25380                   | 4.38              |
| 4            | 328           | 345                        | 25380                   | 6.25              |
| 5            | 340           | 354                        | 25380                   | 9.38              |
| 6            | 360           | 462                        | 25380                   | 6.25              |
| 7            | 385           | 345                        | 25380                   | 6.25              |
| 8            | 380           | 112                        | 25380                   | 3.13              |
| 9            | 385           | 69                         | 25380                   | 4.38              |
| 10           | 360           | 43                         | 25380                   | 3.75              |
| 11           | 390           | 501                        | 25380                   | 12.5              |
| 12           | 365           | 575                        | 25380                   | 10                |
| 13           | 400           | 253                        | 25380                   | 11.88             |
| 14           | 350           | 49                         | 25380                   | 3.13              |
| 15           | 385           | 40                         | 25380                   | 1.25              |
| 16           | 405           | 627                        | 25380                   | 37.5              |
| 17           | 395           | 594                        | 25380                   | 5                 |
| 18           | 383           | 137                        | 25380                   | 5.63              |
| 19           | 393           | 64                         | 25380                   | 4.38              |
| 20           | 390           | 96                         | 25380                   | 5.63              |
| 21           | 395           | 737                        | 25380                   | 18.75             |
| 22           | 388           | 733                        | 25380                   | 21.88             |
| 23           | 398           | 548                        | 25380                   | 18.75             |
| 24           | 392           | 455                        | 25380                   | 3.13              |
| 25           | 402           | 63                         | 25380                   | 5                 |

The increase of the water content and number of the suspension in the slurry caused the fluidity to increase. The water content of the slurry was controlled to be 0.9–1.3%, with a suspension number of 1–5. With a suspension number of 1, the fluidity of the slurry was the lowest, and with a suspension number of 5, the fluidity was the highest.
Cement ratio, of factors on fluidity is ranked in the following order: water analysis result shows that the significance of the influences on the fluidity decreases with the increase of the contents of other gel materials, especially the reinforcing agent content. The range of cement ratio is maximum (A5), the fluidity is significantly greater than the fluidity of A1–A4. From the comparison of Figure 5, it is clear that, when the water–cement ratio remains constant, the fluidity decreases with the increase of the contents of other gel materials, especially the reinforcing agent content. The range analysis result shows that the significance of the influences on factors is fluidity is ranked in the following order: water–cement ratio (R_A) > reinforcing agent content (R_B) > accelerator content (R_C) > expansion agent content (R_D) > suspension agent content (R_E). Clearly, the water–cement ratio and the reinforcing agent content have significant effects on fluidity, while the impacts of other factors on fluidity are relatively weak.

Figure 5 illustrates the curves of relationships between fluidity and factors in the orthogonal test. The increase of water–cement ratio promotes the relative content of water in the slurry, which conduces to the full suspension and diffusion of cement particles. When the water–cement ratio is greater than 1.1, the effective fluidity of the sealing material changes slightly; that is, the diffusion radius of the uniform slurry tends to stabilize. The main reason is as follows: with the increase of water content of the sealing material, more water is adsorbed on the surface of the cement particles in the slurry, and then the cement particles absorbe water through capillary salt absorption. As the water invades, the relative humidity inside the slurry rises and the pore water tends to be saturated. With continuous hydration of the slurry, the capillary adsorption force of the thin layer of the hydration products of mineral components in the sealing material covers the surface of the cement particles, and then the internal cement particles absorb water through capillary salt absorption. As the water invades, the relative humidity inside the slurry rises and the pore water tends to be saturated. With continuous hydration of the slurry, the capillary adsorption force of the thin layer of the hydration products of mineral components in the sealing material covers the surface of the cement particles, and then the internal cement particles absorb water through capillary salt absorption.

As a result, the cement particles become uniformly dispersed, and the flow resistance between the cement particles weakens. The reinforcing agent, as the filling material, reduces the relative water–cement ratio to some extent, which explains why the fluidity of the sealing material decreases with the increase of the reinforcing agent content.

The influences of accelerant and alkali activator contents on fluidity increase initially and decrease later. The most important factor that contributes to this phenomenon is that the rapid hardening effect of the accelerant and the early strength effect of the alkali activator accelerate the hydration process of the cement slurry. In addition, the specific surface area of the accelerant is larger than that of PC, so that the sealing material relies on the particle surface to adsorb more water, thus reducing the fluidity of the slurry. The suspension agent content and the expansion agent content have the weakest influences on fluidity. The suspension agent mainly plays the role of filling and dispersing the cement particles. Therefore, the ratio of the sealing material with suitable fluidity is A1, B1, C1, D1, E1; that is, the water–cement ratio is 1.1, the accelerator content is 25%, the alkali activator content is 5%, the suspension agent content is 5%, the expansion agent content is 0.2%, and the reinforcing agent content is 4%.

3.2. Analysis on Factors Influencing the Setting Time.

Figure 6 presents the variation of setting time in the orthogonal test. As disclosed by Figures 6 and 7, overall, the setting time shortens as the accelerator content increases. Such a result suggests that the accelerant promotes hydration condensation of PC. It is mostly because the retarding component CaSO₄ in PC and the C₃₆AsS′ mineral in the accelerant are hydrated to produce highly active Al(OH)₃ that reacts with Ca(OH)₂ to produce ettringite, which strengthens the condensation of the slurry. The thin layer of the hydration products of mineral components in the sealing material covers the surface of the cement particles, and then the internal cement particles absorb water through capillary salt absorption. As the water invades, the relative humidity inside the slurry rises and the pore water tends to be saturated. With continuous hydration of the slurry, the capillary adsorption force of the thin layer of the hydration products becomes smaller. In this case, water in the slurry mainly resorts to gravity for diffusion and transmission, so that the unhydrated cement particles continue to hydrate and fill the pores of the slurry. Consequently, the setting time of the sealing material extends with the growth of the water–cement ratio.

As shown in Figure 7, the contents of the reinforcing agent, expansion agent, and alkali activator have insignificant influences on the setting time. The range analysis result reveals the order of the significance of the influences of factors on setting time: accelerator content (R_A) > water–cement ratio.

Figure 2. Performance testing of the sealing material.

Figure 3. Microstructure analysis of the sealing material.

Figure 4. Variations of fluidity in the orthogonal test.
The reinforcing agent has high pozzolanic activity, which promotes the hydration of the cement materials to produce Ca(OH)$_2$ crystals and more amorphous gel hydration products. The process of filling the microscopic pore structure of the slurry slightly prolongs the setting time. Furthermore, the expansion agent (aluminum powder) reacts with H$_2$O and Ca(OH)$_2$ to form H$_2$O (2Al + 2OH$^-$ + 2H$_2$O $\rightarrow$ AlO$_2$ + H$_2$↑) and CaSO$_4$, and the C$_3$A minerals react to form ettringite crystals (C$_3$A + 3(CaSO$_4$·2H$_2$O) + 2Ca(OH)$_2$ + 24H$_2$O $\rightarrow$ 3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O). Their combination extends the hydration process of the slurry.

As a result, the setting time of the sealing material is slightly shortened with the increase of the suspension agent content. Therefore, the ratio of the sealing material with effective setting time is $A_5B_2C_1D_5E_3F_4$; that is, the water–cement ratio is 1.3, the accelerant content is 30%, the alkali activator content is 3%, the suspension agent content is 5%, the expansion agent content is 0.4%, and the reinforcing agent content is 3%.

3.3. Analysis on Factors Influencing the Expansion Rate. Figure 8 exhibits the variations of expansion rate in the orthogonal test. It can be observed from Figures 8 and 9 that, overall, the expansion rate rises with the increase of the expansion agent content ($A_1$). This is mainly because in the alkaline slurry, aluminum powder reacts to produce Al(OH)$_3$
gel and H₂. The reaction consumes Ca(OH)₂ gel, a hydration product of cement in the sealing material, and meanwhile produces more C−S−H gel. The crystal structure is therefore wrapped by hydration products such as gel, and then the generated gas is sealed inside the stone body, showing an expansion effect. The C₄A₃S′ mineral contained in the accelerant reacts with the dissolved alkali activator to form radially arranged ettringite and layered Al(OH)₃ gel, and the crystal expansion effect is formed by crystal and gel hydration products.

As shown in Figure 9, the range analysis result shows that the significance of the influences of factors on expansion rate is ranked in the following order: expansion agent content (R₈) > accelerator content (R₉) > water−cement ratio (R₆) > suspension agent content (R₇) > reinforcing agent content (R₅) > alkali activator content (R₄). The expansion agent content and the accelerator content have notable effects on expansion rate, while the impacts of other factors are limited.

As mentioned in the above analysis, the setting time of the slurry lengthens with the increase of water−cement ratio, which is beneficial for the hydration of fine cement particles in the material. Layered montmorillonite minerals in bentonite will expand after absorbing water. Besides, they boast good adhesion and dispersion properties. These properties enable them to improve the viscosity of the sealing material, increase the density of the grout film and the stability of foam, and exert a certain moderating effect on the expansion performance of the slurry. As the reinforcing agent content increases, more SiO₂ is provided to react with the dissolved alkali activator to form the C−S−H gel, offering more nucleation sites for the formation of hydration products. Therefore, the ratio of the sealing material that endows the consolidation body with microexpansion performance is A₃B₁C₁D₁E₁F₁; that is, the water−cement ratio is 1.1, the accelerator content is 50%, the

![Figure 7. Curves of relationships between the setting time and factors for the sealing material.](https://doi.org/10.1021/acsomega.2c02334)

![Figure 8. Variations of expansion rate in the orthogonal test.](https://doi.org/10.1021/acsomega.2c02334)
alkali activator content is 3%, the suspension agent content is 3%, the expansion agent content is 0.5%, and the reinforcing agent content is 2%.

3.4. Multiple Linear Regression Analysis. According to the range analysis on orthogonal test results, the two primary factors influencing the performance indicators of the sealing materials were selected. The response surfaces of the main influencing factors on the performance indicators (fluidity, setting time, and expansion rate) were simulated by adopting Design Expert 11 software, and the corresponding predictive regression model was established. Analysis of variance was performed to determine the significance of each model term. The model statistical significance was checked by $F$. The model

| model | sum of squares | degrees of freedom | mean square | $F_{-0.05}$ | P-value | $R^2$ |
|-------|---------------|--------------------|-------------|-------------|---------|-------|
| $Y_t$ | regress       | 3658.86            | 3           | 1219.62     | <0.0001 | 0.9084|
|       | residual      | 369.14             | 12          | 30.76       |         |       |
|       | total         | 4028               | 15          |             |         |       |
| $Y_{s1}$ | regress   | $4.546 \times 10^5$ | 5           | 909 29.85   | <0.0001 | 0.9777|
|         | residual     | 1036.65            | 10          | 1036.65     |         |       |
|         | total        | $4.65 \times 10^5$ | 15          |             |         |       |
| $Y_{s2}$ | regress   | $6.711 \times 10^5$ | 5           | 1.342 $\times 10^5$ | <0.0001 | 0.9715|
|         | residual     | 19709.07           | 10          | 1970.91     |         |       |
|         | total        | $6.908 \times 10^5$ | 15          |             |         |       |
| $Y_e$  | regress       | 504.64             | 9           | 56.07       | <0.0001 | 0.985 |
|       | residual      | 7.71               | 6           | 1.28        |         |       |
|       | total         | 512.35             | 15          |             |         |       |

Figure 9. Curves of relationships between the expansion rate and factors for the sealing material.
fit was checked by $R^2$. Subsequently, the optimal ratio was selected through the response surface.

RSM was applied to identify the best combination of experimental parameters (water−cement ratio, accelerant content, expansion agent content, and reinforcing agent content) for the fluidity, setting time, and expansion rate of the sealing material. The performances of the sealing material were predicted by multiple linear regression analysis used to represent the response surface $Y$. In addition, the expression can be written as 1 and 2

$$Y = a_0 + \sum_{i=1}^{k} a_i X_i + \sum_{i=1}^{k} a_{ij} X_i^2$$

(1)

$$Y = f(A, B, C, D, E, F)$$

(2)

where $Y$ is the response value, $a_0$ is the intercept, $a_i$ is the linear coefficient, $a_{ij}$ is the quadratic coefficient, and $X_i$ is the interaction effect. $X_i$ and $X_j$ are the independent variables, and $X_i X_j$ and $X_i^2$ represent the interaction and quadratic terms, respectively. $A$ is the water−cement ratio, $B$ is the accelerant content, $C$ is the alkali activator content, $D$ is the suspension agent content, $E$ is the expansion agent content, and $F$ is the reinforcing agent content.

### 3.4.1. Building Regression Models

The model statistical analysis of variance results for fluidity ($Y_f$), setting time ($Y_s$), and expansion rate ($Y_e$) are given in Tables S. Equations 3−6 are four fitting models of the multiple linear regression analysis ($Y_f$, $Y_{s1}$, $Y_{s2}$, and $Y_e$), respectively. The fitted linear regression coefficients ($R^2$) are 0.9084, 0.9777, 0.9715, and 0.985, respectively. Meanwhile, the significance levels of variance analysis for four models are all <0.05 ($P$-value <0.05), indicating that the models are highly statistically significant.

$$Y_f = 382.88 + 13.25A - 14.69F + 14.06AF$$

(3)
The saliency of the above models was evaluated by conducting goodness-of-fit tests. Figure 10 presents the relationship between the predicted values and the actual values; it can be seen that the correlation between the variables and fluidity ($Y_f$), setting time ($Y_s$), and expansion rate ($Y_e$) can be described with the empirical model, providing evidence for the validity of the regression model. Color point is represented by the value of fluidity ($Y_f$), initial setting time ($Y_{s1}$), final setting time ($Y_{s2}$), and expansion rate ($Y_e$).

### 3.4.2. Analysis on Response Surface

The effect of variables on the response is shown in the 3D response surface and contour plots for the fluidity of the sealing material; both plots are the graphical representation of the regression equation.

Figure 11 shows the effect of interaction between the water–cement ratio and the reinforcing agent content on the fluidity of the sealing material, and it can be observed from the contour plots that the fluidity increases gradually with the increase of the water–cement ratio and the decrease of the reinforcing agent content, which verifies the results of the orthogonal test. The main reason is as follows: sufficient water makes the cement particles in the material disperse uniformly, and the filling material increases the friction resistance during the particle flow in the slurry. The water–cement ratio and the fluidity of the experimental values are proportional, while the reinforcing agent content is oppositely proportional. As is shown in Table 3, the model of fluidity is significant ($P$-value <0.0001).

$Y_{s1} = 134.81 - 161.68B + 164.03A - 34.81AB + 55.85B^2$

+ 105.51A^2

(4)

$Y_{s2} = 227.51 - 218.55B + 196.57A - 12.87AB$

+ 25.61B^2 + 109.62A^2

(5)

$Y_e = 2.72 + 25.28E - 12.3B + 6.24EB - 2.82E^2$

+ 8.92B^2 + 13.59E^2B + 10.2EB^2 - 29.09E^3$

+ 4.31B^3

(6)

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3.4.2. Analysis on Response Surface. The effect of variables on the response is shown in the 3D response surface and contour plots for the fluidity of the sealing material; both plots are the graphical representation of the regression equation.

Figure 11 shows the effect of interaction between the water–cement ratio and the reinforcing agent content on the fluidity of the sealing material, and it can be observed from the contour plots that the fluidity increases gradually with the increase of the water–cement ratio and the decrease of the reinforcing agent content, which verifies the results of the orthogonal test. The main reason is as follows: sufficient water makes the cement particles in the material disperse uniformly, and the filling material increases the friction resistance during the particle flow in the slurry. The water–cement ratio and the fluidity of the experimental values are proportional, while the reinforcing agent content is oppositely proportional. As is shown in Table 3, the model of fluidity is significant ($P$-value <0.0001).

Figure 12 (Figure 13) shows the effect of interaction between the accelerator content and the water–cement ratio on the initial (final) setting time of the sealing material, and it can be observed from the contour plots that the initial setting time and the final setting time have the same trend as the variables change. The setting time shortens with the increase of the accelerator content and the decrease of the water–cement ratio, which is in line with the results of the orthogonal test. One contributing factor is that the hydration of $C_A$3$S'_3$ mineral in the accelerator weakens the retarding effect of $CaSO_4$ after the dissolution of PC and meanwhile produces highly active $Al(OH)_3$. Afterward, $Al(OH)_3$ reacts with $Ca(OH)_3$ to form hydration products such as ettringite, which facilitates the setting of the slurry. Another factor is that the decrease of the water content of the slurry causes the decline of the water content of the thin layer of flocculated hydration products formed by capillary salt absorption through the surface. The reduction of pore water also accelerates the setting of the slurry. The water–cement ratio and the initial (final) setting time of experimental values are proportional, while the accelerator content is oppositely proportional. As is shown in
Figure 14. Response surface and contour plots indicating the effect of interaction between the expansion agent content and the accelerator content on the expansion rate of the sealing material. The number inside the contour plots indicates the expansion rate.

Table 3, the model of initial (final) setting time is significant (P-value <0.0001).

Figure 14 shows the effect of interaction between the expansion agent content and the accelerator content on the expansion rate of the sealing material, and it can be observed from the contour plots that the expansion rate rises first and then falls with the increase of the expansion agent content, but the relationship between the expansion rate and the accelerator content is complicated, which agrees with the results of the orthogonal test. The main reason for such a difference is that in the alkaline slurry of the sealing material, the expansion agent first reacts to produce Al(OH)$_3$ and H$_2$ and continuously generates Ca(OH)$_2$ and C–S–H gel at the same time. The small bubbles generated by gel encapsulation and storage endow the consolidation body with an expansion effect. However, the C$_4$A$_7$S$'$ mineral in the accelerator reacts with the dissolved alkali activator to form radially arranged ettringite crystals and layered aluminum adhesives. The crystal structure after hardening limits the development of the expansion effect of the consolidation body. As shown in Table 3, the model of expansion rate is significant (P-value <0.0001).

3.5. Optimization of Material Ratio. According to the orthogonal test results, the preliminarily optimized material ratios are A$_1$B$_1$C$_1$D$_1$E$_1$F$_1$, A$_2$B$_2$C$_2$D$_2$E$_2$F$_2$, and A$_3$B$_3$C$_3$D$_3$E$_3$F$_3$, respectively. According to the range analysis, when the water–cement ratio is 1.1 and the expansion agent content is 4%, the sealing material has good fluidity performance; when the accelerator content is 30% and the water–cement ratio is 1.3, the sealing material corresponds to an appropriate setting time; when the expansion agent content is 0.5% and the accelerator content is 50%, the sealing material exhibits microexpansion performance.

In order to verify the experimental results of range analysis, the regression models of multiobjective optimization are compared. The experimental results, predicted values, and errors are shown in Table 6. The errors of setting time, fluidity, and expansion rate are smaller than 5%, which demonstrates that the test results are highly consistent with the predicted values. The comparison verifies that the model is highly accurate.

The ideal response factors and the predicted values under a fluidity of 360–380 mm, an initial (final) setting time of 60 (80)–80 (100) min, and an expansion rate of 2–12% are shown in Figure 14. That is, when the water–cement ratio is 0.971 and the expansion agent content is 3.202%, the fluidity is 372 mm; when the accelerator content is 57.3% and the water–cement ratio is 1.137, the initial (final) setting time is 66 (98) min; when the expansion agent content is 0.105% and the accelerator content is 32.4%, the expansion rate is 4.33%.

Therefore, considering the fluidity, setting time, and expansion rate, the values of response factors are determined as follows: the water–cement ratio is 1.1, the accelerator content is 50%, the expansion agent content is 0.1%, and the reinforcing agent content is 3% (Figure 15).

4. MICROSTRUCTURE ANALYSIS ON OPTIMIZED MATERIALS

4.1. MICROSTRUCTURE ANALYSIS ON OPTIMIZED MATERIALS

4.1. XRD Analysis. The XRD spectra of the optimized PC materials added with the accelerator, expansion agent, and reinforcing agent are illustrated in Figure 16; all the notations are explained as follows: (a) AFt, (b) Ca(OH)$_2$, (c) C$_3$S, (d) C$_4$S, (e) C$_4$A$_7$S$'$, and (f) CaCO$_3$. As can be seen from the intensity of the diffraction peak,

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Table 6. Experimental Results and Model-Predicted Values

| result | fluidity (mm) | initial setting time (min) | final setting time (min) | expansion rate (%) |
|--------|---------------|--------------------------|------------------------|--------------------|
| test value | 390 | 567 | 733 | 3.13 |
| predicted value | 375 | 573 | 712 | 3.16 |
| error (%) | 3.8 | 1.1 | 2.9 | 0.9 |

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and then the different components of the accelerant, expansion agent, and reinforcing agent were added. The sealing material changed the hydration products of the ordinary cement materials. The latter is consumed by SiO$_2$ to generate the C$-$S$-$H gel, and then these large quantities of the amorphous C$-$S$-$H gel are wrapped on the surface of other crystal products.

**4.2. SEM Analysis.** The microstructures of the optimized materials are illustrated in Figure 17. The results show that the hydration products of the PC materials contain abundant pore structures, and the surface of the particles is covered by layered Ca(OH)$_2$ products, which is a mark of a low hydration degree. This is mainly because the retarding component CaSO$_4$ in PC prolongs the setting time of the slurry and hinders the hydration reaction. After the addition of the accelerator, the pores between the hydration products of the material become smaller. This
indicates that the full hydration reaction of the material produces fine acicular AFt crystals and flake CH crystals. After the addition of the expansion agent, the generated gas is sealed in the stone body, and the expansion effect makes the microstructure of the hydration products more compact, thus improving the original pore structure. After the addition of the reinforcing agent, a large number of C−S−H gel-like hydration products occur on the surface of the material. These reticular or foil-like C−S−H gels with a large specific surface area and strong cementation ability fill in the holes of the three-dimensional spatial reticular skeleton structure to form a cement-based composites with a certain strength.46,47

5. RESULTS AND DISCUSSION

New cement-based sealing materials were prepared in this work, and the optimal ratios of each component were investigated using the orthogonal test.47,48 Then, the regression models and their predicted values were verified by the test data. Furthermore, the microstructure of this optimized material was analyzed by XRD and SEM methods. The main findings are obtained as follows:

1. The orthogonal test results indicate that the most important influencing factors on fluidity, setting time, and expansion rate correspond to the water−cement ratio, the accelerator, and the expansion agent, respectively. In addition, the most influential factor combinations of that are the water−cement ratio and the reinforcing agent, the accelerator content, and the water−cement ratio, and the expansion agent and the accelerator content, respectively.

2. The regression models of this optimized sealing material were established by the RSM method, and the reliability of the predicted values is verified by test data. Furthermore, optimization areas of the predicted values were found by analyzing the interaction of the two response factors. The errors of setting time, fluidity, and expansion rate are smaller than 5%, which indicate that the test results are highly consistent with the predicted values and present a pretty good accuracy of the regression models.

3. According to the performance principle of the sealing material, that is, high fluidity, suitable setting time, and the microexpansion effect, the best performances of the fluidity, the initial (final) setting time, and the expansion rate of the optimized cement-based sealing material can reach 360−380 mm, 60 (80)−80 (100) min, 2−12%, respectively. In addition, the optional proportion corresponding to the above indexes is a water−cement ratio of 1.1, an accelerator content of 50%, an expansion agent content of 0.1%, and a reinforcing agent content of 3%.

4. The microstructure of this optimized cement-based sealing material reveals that the hydration products of PC are transformed from layered Ca(OH)₂ crystals into fine needle-like AFt crystals by the action of the accelerator added.49 Moreover, the addition of the expansion agent and reinforcing agent can promote the generation of a large number of Al(OH)_3 gel, C−S−H gel, and other hydration products, thus leading to a more compact microstructure of this optimized sealing material.

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Notes
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