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Research Article

Study on Modification of Alkali-Free Liquid Accelerator of Mine-Used Wet-Mix Shotcrete

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Compound properties of an alkali-free liquid accelerator are the mainstream of accelerator research and development in the present. Combined with the technical characteristics of wet-mix shotcrete in coal mines, organic high-polymer SWF is used to modify the accelerator because of improving the bond strength of the material and increasing the performance of antisagging. The mechanism of filling and thickening of SWF was analyzed from the aspects of pore characteristics and spatial structure of concrete. Through the determination of setting time, strength, and dispersibility, the optimum dose was determined, and a new style accelerator WIT-1 suitable for wet-mix shotcrete in coal mines was developed and applied on-site. The experimental results show that the addition of SWF increases the dispersibility of the accelerator product and the cohesiveness of concrete under the condition of ensuring strength and setting time, and the effect of modifying the accelerator to reduce the rebound of the wet-mix shotcrete is obvious.

1. Introduction

The accelerator is an admixture for rapid solidification and hardening of concrete in shotcrete, and it increases the primary spraying thickness, reduces material rebound, and reduces dust pollution by accelerating the solidification of spraying materials to improve economic efficiency and meet engineering needs. Domestic and foreign research on the shotcrete technology has always put the accelerator research in a very important position, and in terms of composition and status, the accelerator has underwent a development process from the early alkaline powder accelerator to medium-term low-alkali or liquid accelerator and then to the recent alkali-free liquid accelerator [1–6]. Considering the influence of the accelerator on spraying concrete's mechanical properties, construction performance, and construction methods, the mainstream accelerator is currently developing from a single property towards compound properties [7–10]. Although the most representative alkali-free liquid accelerator in the world has entered the Chinese market, at present more than 90% of China's accelerators are still dominated by the powdery accelerator and liquid accelerator with high alkali contents, which are composed of sodium silicate, sodium aluminate, and sodium carbonate. There is still a big gap between domestic alkali-free liquid accelerator products and foreign products, and there are still many shortcomings especially in improving the overall performance of concrete [1, 11–13].

The development and application of composite performance materials is increasingly widespread [14, 15]. The wet-mix shotcrete technology has just begun to develop in the field of coal production, compared with other industries, due to the small space of the mine work, the complex environment, and so on, and the requirement of mine-used wet-mix shotcrete in reducing the dust and rebound in the spraying process is more urgent [16–19]. Therefore, through the study of compound modification of the accelerator, the comprehensive performance of the existing alkali-free liquid accelerator and the quality of shotcrete are improved and the application of the wet-mix shotcrete technology in the coal mining industry is promoted.

2. Study on the Modified Mechanism

Redispersible emulsion powder (SWF) is a powdery thermoplastic resin prepared from polymer emulsion by the process of spray-drying and subsequent treatment and so on, and the basic components include polymer resins, internal and external additives, protective colloids, and anticaking agents. Take tile adhesive mortar as an example; its preparation and performance study are shown in Figure 1. Due to the excellent properties of SWF in many ways which include increased cohesion and flexibility, it is widely used in the modification of hydraulic products such as cement [20–22].

Teng's experiment [23] shows that the addition of a small volume of SWF in the mortar can significantly improve the mortar bond strength, bending strength, and compressive strength, and the flexibility of modified mortar is also improved with the increase of SWF volume. Zurbriggen et al. [24] point out that SWF can maintain the properties and functions of organic adhesives in the emulsion state and improve the strength and adhesion of the composite paste. SWF can form a strong and soft film at the mortar/tile interface and improve bond strength and the quality of shotcrete.

From the consideration of improving the properties of wet-mix shotcrete, the polymer composition of SWF has good dispersibility and film-forming property so that it can easily form a film at the interface between the pores of the concrete and the matrix to form a small polymer phase to improve the bond strength. The internal organic adhesive composition of SWF can improve the antisagging property and instantaneous adhesion property of the concrete. The buffer layer can be formed as soon as possible by increasing the bond force between the cement slurry and the aggregate, thereby effectively promoting the mechanical energy conversion of the high-speed concrete slurry. Finally, the rebound and dust of the sprayed period are reduced after the buffer layer is formed. Due to the wet-mix shotcrete technology's requirement for concrete workability and need for underground construction operation, it is not advisable to add SWF directly to fresh concrete, so adding an SWF having a specific function to the accelerator and constituting a composite accelerator with excellent properties promote the quality of shotcrete.

3. Experimental Study on Modification of Liquid Accelerator of Wet-Mix Shotcrete

3.1. Experimental Materials and Mix Ratio. The experimental cement is selected from PO42.5 ordinary Portland cement made by Shandong Liuyuan Cement Co., Ltd., and the sand is selected from medium sand with a fineness modulus of 2.8. The mass ratio of cement to sand is 1 : 1.5, and the water-cement ratio is 0.5, in line with JC477-2005 [25].

At present, the main components of accelerator varieties can be roughly divided into types of aluminum oxide clinker plus carbonate, sulphoaluminate, water glass system, and so on. A variety of alkali-free liquid accelerator samples are selected at the early stage of the experiment [4, 26]. According to the requirements of China's building materials industry standard JC477-2005 [25], the properties of the paste with the accelerator and the hardened mortar should meet the requirements given in Table 1 [27]. Three kinds of accelerator samples are optimized as the modified carriers through the cement adaptability experiment, named as accelerators A, B, and C, respectively.

By measuring the setting time, the volume of A, B, and C for the sample of the accelerator which meets the production requirements is 10%, 8%, and 10% of the cement quality, respectively. The volume of each accelerator sample in accordance with the actual application of setting time is greater than that of the recommended volume. Due to many factors affecting the setting time of the accelerator, especially the changes of the properties of cement, the volume of the accelerator in actual construction should be determined by the field test.

According to the JC477-2005 standard [26], the water volume of the accelerator is calculated according to the determination result of the solid volume; the volume determination of the accelerators A, B, and C is shown in Table 2.

Modifier SWF is divided into two major categories: homopolymers and copolymers, in which the dominant component is the polymer powder. The SWF selected for modification is the VAc/ethylene copolymer (Industrial Grade; Shanxi Sanwei Group Co., Ltd.), and the main performance parameters are shown in Table 3.

In general, the volume of SWF added ranged from 1% to 10% of the mass fraction of the accelerator; according to the enhancement of strength and adhesion effect, the SWF volume of the modified accelerator is determined as 0, 1%, 2.5%, and 5% of the practical application of the accelerator. According to the JC477-2005 [25] standard setting time test method and strength test method, we can determine the best modified samples by setting time and strength; at the same time, the correction effect was verified by the rebound rate test by the field test.

3.2. Setting Time Experiment. In Figures 2 and 3, the results of the setting time of the modified accelerator show that the influence of SWF on the initial setting time of the three accelerators is different: in Figure 2, the initial setting time of accelerator A decreases first and then increases with the increase of the volume of SWF, the initial setting time of accelerator B first decreases, increases, and then decreases with the increase of the volume of SWF, and the setting time of accelerator C increases significantly with the increase of the volume of SWF. The comprehensive comparison shows that the addition of a large volume of SWF generally prolongs the initial setting time of the accelerator. However, in Figure 3, the SWF has a more obvious effect on the final setting time of the accelerator and generally increases the

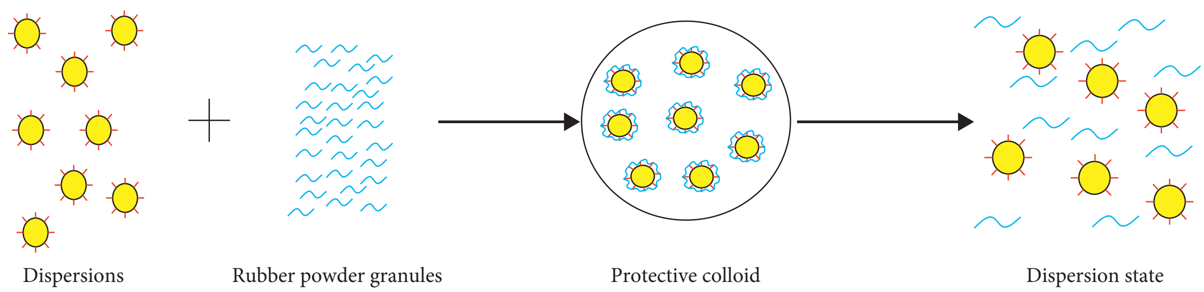

Figure 1: Preparation and properties of the adhesive mortar.

Table 1: Performance requirements of the paste with the accelerator and hardened mortar.

Product grade	Initial setting time (min)	Final setting time (min)	1 d compressive strength (MPa)	28 d compressive strength ratio (%)
First grade	≤3.0	≤8.0	≥7.0	≥75
Qualified products	≤5.0	≤12.0	≥6.0	≥70

Table 2: Solid volume and setting time measurement results.

Name of the sample	Volume (%)	Solid volume (%)	Initial setting time (s)	Final setting time (s)
A	10	47.99	420	540
B	8	40.62	208	517
C	10	48.85	280	440

Table 3: Performance parameters.

Nonvolatile matter (%)	Ash (%)	Average size (μm)	50% viscosity of water solution (Pa·s)	pH value	Appearance
≥98.0	8–12	85 ± 15	2.0–5.0	5–8	White powder

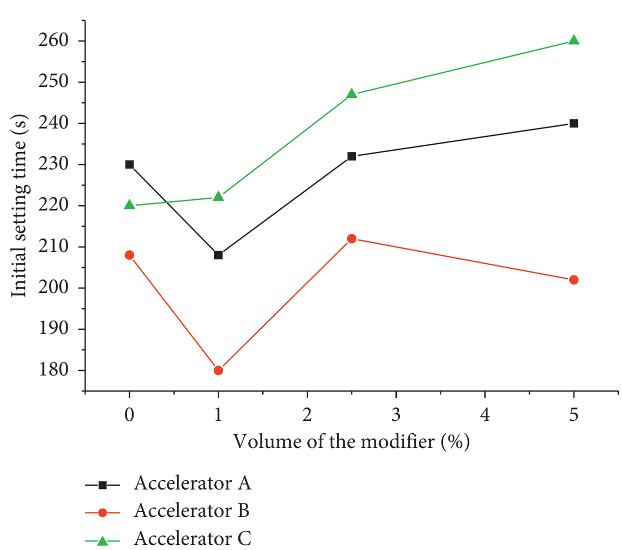

Figure 2: The effect of SWF volume on initial setting time.

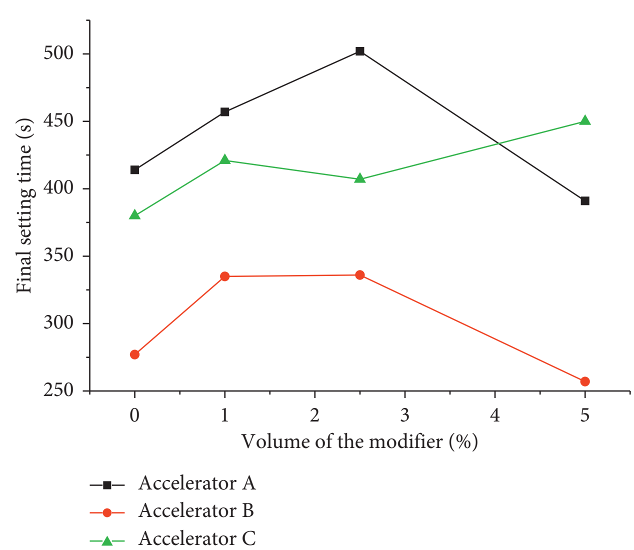

Figure 3: The effect of SWF volume on final setting time.

final setting time. Wang and Wang's research [28] also shows that the initial hydration rate of the cement slowed down after adding the SWF, but the polymer film can partially or completely encapsulate the cement particles so that the cement is fully hydrated and various properties are improved. The experimental results show that the setting time is the longest at 502 s under experiment volume, which is still within the range of the qualified products. According to the influence of SWF on the setting time of the above three accelerator samples, it is considered that SWF generally has an increasing effect on the setting time of the accelerator, but the degree of influence is not significant.

3.3. Compressive Strength Test. Table 4 shows the compressive strength of the accelerator samples at 1 d and 28 d and standard deviation of compressive strength. It can be seen that the standard deviation of 28 d compressive strength of the sample is obviously greater than that of 1 d compressive strength, but all are within a reasonable range. 1 d compressive strength regularity of the sample is not obvious, and through the long-term 28 d strength analysis, the following rules can be seen: in Figure 4, the 28 d compressive strength of accelerators A and B is better than that of C. The compressive strength of accelerators A and C decreases with the addition of SWF. The effect of accelerator C is more obvious; when SWF is added to 5%, its 28 d compressive strength ratio drops sharply below 75%. For accelerator B, the compressive strength first increases and then decreases with the addition of SWF. There is an optimum volume for improving the strength; when the volume of SWF is 2.5%, the 28 d compressive strength ratio of the accelerator reaches 101.00%, which is slightly higher than the maximum compressive strength ratio of accelerator A. The posttreatment strength improvement effect of the modified accelerator is obvious.

During the experiment, the cohesiveness of the cement slurry was observed after the main accelerator considered was added. Since the cement paste instantly becomes very viscous with almost instantaneous loss of plasticity after being added into the accelerator, it cannot be used conventionally for measuring viscosity to characterize the degree of cement paste viscosity. So the viscous degree of cement paste was observed by observation; during the test, we found that, with the increase of the volume of SWF, the cement paste becomes more viscous, which has good effect on increasing the cohesiveness of shotcrete, reducing the shotcrete rebound, and increasing the thickness of the primary spraying. Considering the influence of SWF on the setting time, compressive strength, and cohesiveness of the accelerator sample, the properties of the modified accelerator in group B are more balanced. Further analysis and determination of the accelerator in group B determine the optimum volume.

Table 4: 1 d and 28 d compressive strength of the modified accelerator and standard deviation of compressive strength.

Types	Compressive strength and standard deviation				
	SWF[a] (%)	1 d[b] (MPa)	σ^c (%)	28 d[d] (MPa)	σ^e (%)
Accelerator A	0	9.1	0.36	38.7	3.45
	1	8.9	0.45	38.8	1.74
	2.5	8.4	1.01	34.5	2.35
	5	7.8	1.06	30.9	1.46
Accelerator B	0	8.6	0.41	35.3	2.31
	1	8.9	0.67	36.4	1.57
	2.5	8.1	0.55	39.6	1.88
	5	7.2	0.79	39.1	2.03
Accelerator C	0	8.8	0.63	31.1	3.12
	1	8.4	0.48	30.7	2.94
	2.5	8.5	1.23	30.6	2.12
	5	8.1	0.44	29.9	1.56

[a]The SWF volume range is from 0% to 5% of the accelerator mass fraction; [b]the 1 d compressive strength of the modified accelerator; [c]the standard deviation of 1 d compressive strength; [d]the 28 d compressive strength of the modified accelerator; [e]the standard deviation of 28 d compressive strength.

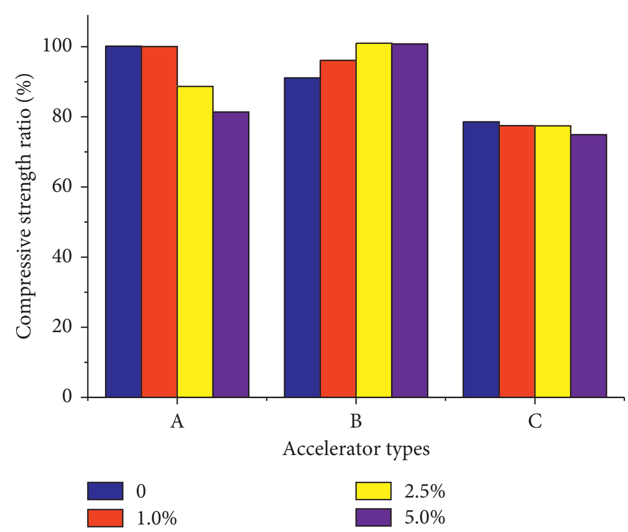

Figure 4: Bar graph of 28 d compressive strength ratio of the modified accelerator.

3.4. Surface Tension Experiment. Surface tension is the free energy per unit area, which is the minimum energy required to form or expand an interface per unit area, which plays a vital role in the physicochemical phenomena of the liquid surface. The research shows that reducing the surface tension can increase the dispersibility of the accelerator. The smaller the surface tension, the higher the collision-agglomeration efficiency. From the consideration of the construction technology of wet-mix shotcrete, reducing the surface tension of the accelerator can improve the sprayed dispersion of the accelerator and improve the ability of the liquid particles to capture the concrete particles, thereby enhancing the quick setting and bonding effect of concrete and improving the quality of shotcrete [21]. Therefore, the surface tension of the modified type B accelerator samples was measured.

By measuring the surface tension of the accelerator sample in group B, in Table 5, it was found that the addition of SWF reduced the surface tension of the accelerator sample. The surface tension decreased significantly with the increase of the modifier volume. When the volume of SWF was 5%, the tension of the accelerator sample reduced to 43.875 mN/m. However, from the practical production, it is not conducive to the delivery of the accelerator in the wet-spraying pipe when the volume of SWF is too large, and the workability of the shotcrete will be affected. Therefore, considering synthetically the influence of the SWF on the sample setting time, compressive strength, cohesiveness, and workability, the optimal modified accelerator was determined to be of group B with 2.5% SWF volume and named as WIT-1.

Table 5: Statistical table of measurement results of surface tension and contact angle.

Modifier volume (%)	Surface tension (mN/m)			Average surface tension (mN/m)
0	69.75	70.292	71.457	70.500
1.0	65.208	64.125	63.917	64.417
2.5	55.333	52.958	52.292	53.528
5.0	43.708	44.167	43.75	43.875

3.5. Modification Mechanism Analysis. According to the experimental results and combined with the hydration reaction of cement, the mechanism of action of SWF is as follows: the redispersed fine polymer particles are evenly dispersed after SWF and accelerator are mixed evenly. After mixing with concrete by spraying, these polymer particles gradually form a cement gel after initial hydration. The liquid phase is hydrated by the formation of saturated calcium hydroxide, and the polymer particles are deposited on a part of the surface of the cement gel/unhydrated cement particle mixture. As the cement hydration polymer particles are gradually confined within the pores, a dense layer of deposits is formed on the cement gel/unhydrated cement particle mixture and the surface of aggregates and gradually gathered to form a continuous network modifier membrane structure in three dimensions, which improves the compact degree of the interface transition region. Hydration products, aggregate surface, and cement stone form a continuous space and form a continuous and dense matrix structure, which increases the contact area between the different particles within the cement stone. This structure improves the compact degree of the interface transition region and also plays the role of bridging when it is subjected to tensile stress and effectively absorbs and transfers energy, thus improving the concrete strength. However, with the increase of the volume of modifier, the air entraining effect of the surfactant compositions on the modifier is prominent, which leads to a higher air entrainment content. And the bubble structure introduced is not good, resulting in a decrease of compressive strength of the sample.

The phase state of SWF in cement mortar was observed by SEM (scanning electron microscope) [28], and we can see that the dispersed small modifier particles can be evenly dispersed in the slurry after the SWF and fresh concrete gel composition are sprayed and mixed. The addition of admixtures improves the quality of shotcrete. The pore structure of 7 d age test block was determined by the surface area and pore radius analyzer (SSA-4200) manufactured by Petri Electronic Co., Ltd. The line chart of pore radius and adsorption volume percentage is shown in Figures 5 and 6. The pore radius was measured by the surface pore analyzer below 200 nm (2000 Å).

Through the test results of specific surface area and pore radius, we can see, in Figures 5 and 6, that the single average pore radius (with BET specific surface area), BJH desorption average pore radius, BJH adsorption most probable pore radius, BJH desorption most probable pore radius, and other test data have been significantly reduced in the pore structure of the test block with modifier. It indicates that the pore structure of the material is changed after the incorporation of the modifier and develops toward the micropore. According to the method of grading holes proposed by an academician Wu [29], the pores of cement stone are divided into four grades: innocuous holes (diameter less than 20 nm), fewer holes (diameter 20–50 nm), harmful holes (diameter 50–200 nm), and more harmful holes (diameter greater than 200 nm). Using the analysis of specific surface area, we can see that the pore structure of the material is changed after the incorporation of SWF, and the pore distribution of the sample develops toward the micropore of pore reduction.

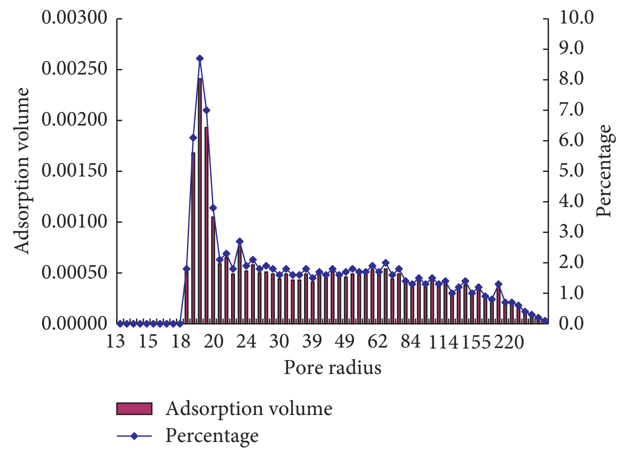

Figure 5: Line chart of pore radius and adsorption volume percentage (without modifier added).

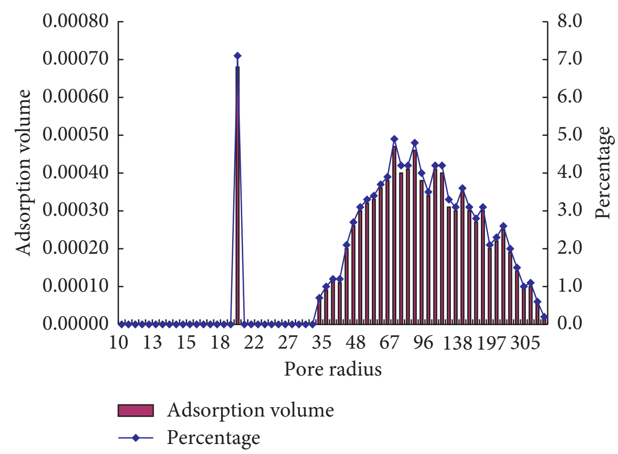

Figure 6: Line chart of pore radius and adsorption volume percentage (with modifier added).

4. On-Site Experiment

The industrial test of the WIT-1 accelerator was carried out on the driving district face of a mine south wing belt lane. This experiment uses PO42.5 ordinary Portland cement. River sand is used as the fine aggregate; the coarse aggregate is selected from the washed gravel and pebble block, and the maximum size of coarse aggregates does not exceed 12 mm. Their physical properties are shown in Table 6. The density of

Table 6: Physical properties of concrete materials.

Concrete materials	Sizes	Bulk density (g/cm^3)	Fineness modulus	Elastic modulus (GPa)	Compressive strength	
					3 d	28 d
Cement	≤60 μm	3.0	Qualified	—	29.8 MPa	55.8 MPa
Fine aggregate	≤3 mm	2.58	2.81	0.21	—	
Coarse aggregate	4–12 mm	2.65	5.68	0.23	—	

shotcrete cement is fixed at 440 kg/m^3, and the water-cement ratio is fixed at 0.50. The shotcrete ratio is shown in Table 7.

According to GB50086-2015 [30] for on-site shotcrete rebound rate determination [31], dust concentration, and compressive strength test, the standard test block is made by the method of cutting the size of the shotcreting board on-site.

The results of the strength test show that the 28 d compressive strength of concrete with the accelerator before and after modification is 27.2 MPa and 27.5 MPa, respectively, which is slightly lower than that of 28.6 MPa without the accelerator sample. The compressive strength ratios are 95% and 96%, respectively. The 28 d bending strength of concrete with the accelerator before and after modification is 8.0 MPa and 8.1 MPa, respectively, which is also slightly lower than that of 8.3 MPa without the accelerator sample. The compressive strength ratios are 96% and 97%, respectively, which meet the technical specifications as a whole.

In Figure 7, the results of the dust test show that the accelerator can significantly reduce the volume of dust produced by shotcrete. Compared with the unmodified accelerator, the dust production of the modified accelerator is more reduced near the spray personnel area, which shows that the viscosity and elastic properties play a role in reducing dust. In Figure 8, the results of the rebound test show that the rebound rate of concrete sidewalls (two gangs) after application of the accelerator is not more than 15% and the arch is not more than 25%, both of which are in line with the characteristics of a rapid drop of accelerator; especially after mixing with concrete, viscosities and bond strength are significantly enhanced. The rebound rate difference between the unmodified accelerator and the modified accelerator is about 30% lower than that of the unmodified accelerator, indicating that the viscous component increases the adsorption force of concrete between each other, and the concrete and roadway walls can effectively reduce concrete rebound of the ministry, which is suitable for underground production needs.

The total cost of shotcrete with the WIT-1 accelerator is ¥105 higher than that without accelerator added in per cubic meter. However, the rebound of shotcrete with the WIT-1 accelerator is reduced by about 15% than that without accelerator added in per cubic meter; according to the price of concrete ¥550/m^3 and recovering material loss, cleaning cost, and construction efficiency, the cost is reduced by about ¥110. On considering the cost of rebound material cleaning, construction efficiency, the cost of tunnel maintenance, dust treatment, etc., the spraying cost of adding the WIT-1 accelerator will be further reduced. It is assumed that the

Table 7: Shotcrete mix ratio.

Materials	Water	Cement	Fine aggregate	Coarse aggregate	WIT-1 accelerator
Quality (kg/m^3)	220	440	993	691	35.2

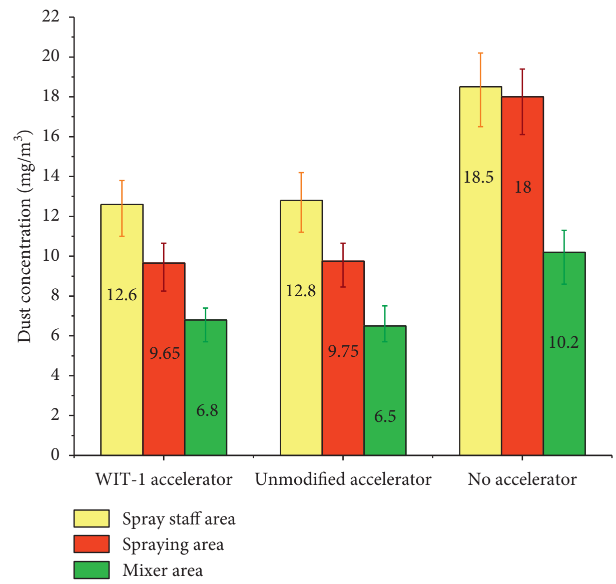

Figure 7: The comparison of three types of shotcrete dust concentration.

length of the shotcrete tunnel is 20000 m. The annual economic benefits can reach more than ¥200,000, so the WIT-1 accelerator is promoted in addition to the macroefficiency and it will also bring direct economic benefits.

5. Results

(1) The organic polymer modifier SWF can improve the bond strength of wet-mix shotcrete and improve the pore characteristics and spatial structure of concrete. The addition of modifier is 2.5% of the accelerator through the formulation experiment. The experimental results show that the setting time of the accelerator is slightly longer for the modifier, but both strength and setting time of the unmodified accelerator meet the requirements of the national standard. The surface tension reaches 53.528 mN/m, and the bond property and dispersibility are remarkably improved.

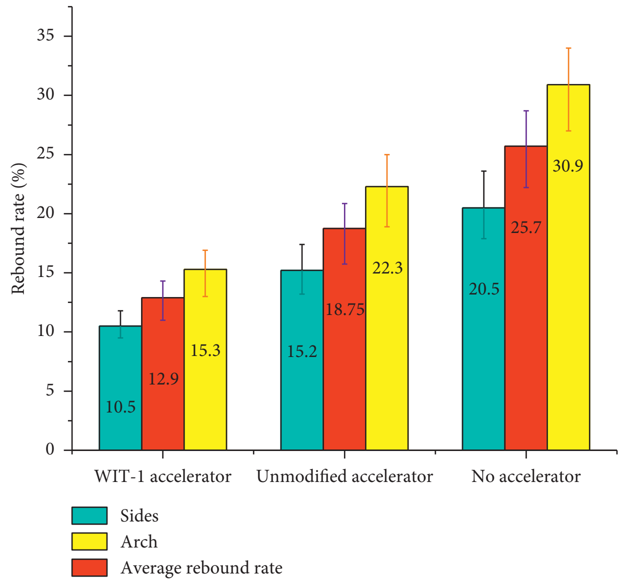

FIGURE 8: The comparison of three types of shotcrete rebound rate.

(2) The field application of the modified accelerator WIT-1 shows that the rebound rate of the modified accelerator is increased by 15% compared with that before the modification, and the modifier has a significant effect on the increase of the viscosity and the reduction of rebound. Both the dust and the strength test results are in line with national standards. The modified accelerator can effectively reduce the wet-spray operation rebound and dust concentration and improve the quality of shotcrete.

(3) Mine-used wet-mix shotcrete in our country is still in the early stages of development, and the reform of wet-mix shotcrete materials and equipment is an inevitable trend of development. Developing the composite properties of high-quality liquid accelerators for better performance and lower price and suitable for coal mine anchor spray operating conditions is beneficial to the popularization and application of wet-mix shotcrete in coal mines.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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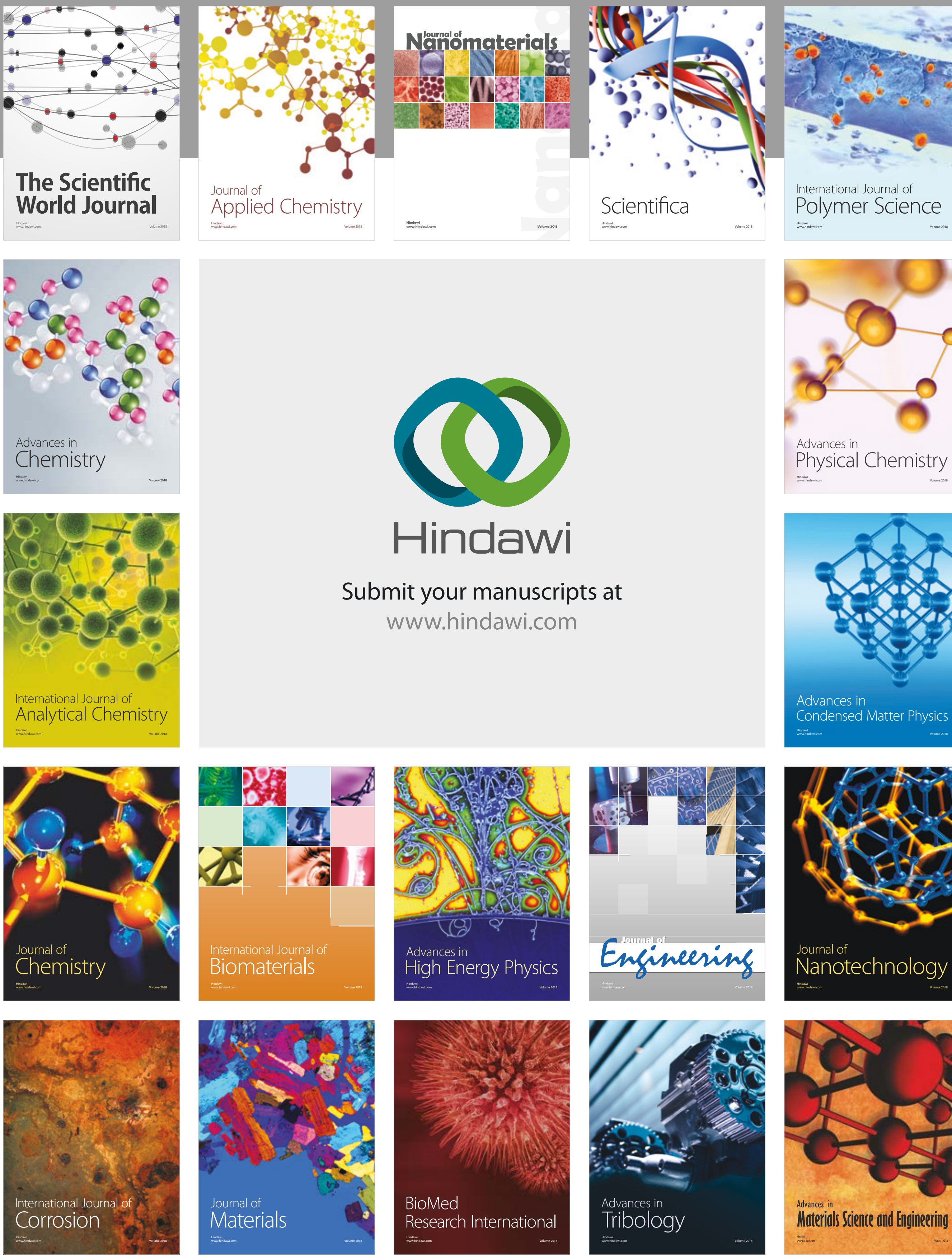
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