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Research Progress and Discussion on Modified Cement-Based Borehole Sealing Materials for Mining

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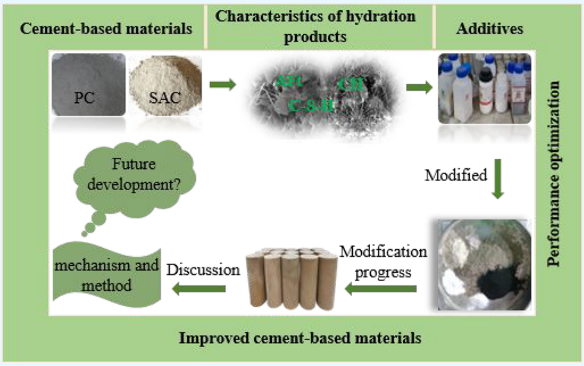
ABSTRACT: As the concept of green mining develops, organic sealing materials are losing popularity in mining, yet the development of inorganic sealing materials for mining has become a research focus. The most common inorganic sealing materials are Portland cement (PC) and sulfate aluminate cement (SAC), but they fail to meet the performance requirements for sealing gas boreholes in complex coal seams due to their limitations. Thus, their performance needs to be modified. This study aims to explore and grasp the current development of inorganic modified cement-based materials from the perspective of improving the performance of cement-based materials of PC and SAC. First, the characteristics of the main hydration products of PC and SAC as well as the effects of these characteristics on their properties were analyzed. Next, the effects of additives such as admixtures, coagulant regulators, and nanomaterials on their properties including hydration properties, coagulation time, and strength were analyzed. Finally, the modification methods and mechanisms were discussed. It is proposed that the optimization of modification effects by various additives is of great practical significance for the development and application of modified PC and SAC in sealing gas boreholes in engineering practice.



1. INTRODUCTION

The coal industry is developing toward deep areas where the coal seam gas occurrence conditions are rather complex and coal and gas outburst disasters occur frequently.[1] Coal seam gas extraction is a fundamental measure to prevent coal and gas outburst, as it can not only quickly eliminate the hazard of coal seam outburst but also realize the utilization of extracted gas as clean energy. Gas extraction efficiency is also affected by borehole sealing materials, borehole sealing technology, and gas extraction methods.[2] The performance of sealing materials is directly related to the quality of borehole sealing and the concentration of extracted gas. Sealing materials shall have good sealing and mechanical properties in order to well seal the borehole leakage channels and reinforce the surrounding rock around boreholes. This ensures a good extraction effect.[3] Therefore, research and development of sealing materials with excellent performance is of important engineering significance for improving gas extraction.

Common organic sealing materials for mining include polyurethane, phenolic foam, urea-formaldehyde, etc. They are expensive and pollute the environment.[4] Moreover, they tend to shrink, foam fast (which makes them uncontrollable), and have poor flowability (which prevents them from effectively diffusing into coal seam fracture), thus failing to seal boreholes tightly.[5,6] Compared with organic sealing materials, inorganic ones boast the advantages of having low cost, multifunctions, and excellent performance and being nontoxic. Hence, they are widely applied in mining activities.

Common inorganic sealing materials, including Portland cement (PC) and sulfate aluminate cement (SAC), are mainly based on cement. These materials are of low cost, are easy access, and are simple to prepare,[7] but they still cannot seal boreholes tightly due to their shortcomings such as long coagulation time, easy shrinkage, and postcuring deformation and poor injectability.[8,9] Considering the shortcomings of cement-based materials, researchers have carried out experiments and engineering applications of modified cement-based materials with inorganic additives as auxiliary materials.[10,11] Modified cement-based materials are superior to traditional inorganic materials in the following way: additives influence the hydration and hardening process of cement by combining with chemical compositions in cement, which in turn changes the physicochemical properties of original cement-based

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Table 1. Basic Chemical Compositions and Hydration Products of PC and SAC[a]

Cement type	Chemical composition	Mineral fraction	Hydration product
PC	Calcium oxide (CaO), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3)	Tricalcium silicate (C_3S), dicalcium silicate, tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF)	Calcium hydroxide (CH), calcium silicate gel (C−H−S), and calcium aluminate (AFt)
SAC	Aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), calcium oxide (CaO), iron oxide (Fe_2O_3), and sulfur trioxide (SO_3)	Calcium sulfoaluminate (C_4A_3S) and dicalcium silicate (C_2S)	Calcium alumina (AFt), alumina gel (AH_3), calcium silicate gel (C−S−H), and monosulfur type calcium sulfate aluminate (AFm)

[a] Note: C_2S: $2CaO{\cdot}SiO_2$, C_3S: $3CaO{\cdot}SiO^2$, C_3A: $3CaO{\cdot}Al_2O_3$, C_4AF: $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, CH: $Ca(OH)_2$, C_4A_3S: $Ca_4Al_6SO_{16}$, C−S−H: $Ca_5Si_6O_{16}(OH){\cdot}4H_2O$, AFt: $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, AH_3: $Al_2O_3{\cdot}nH_2O$ $n < 1$, AFm: $Ca_3AlCaSO_4{\cdot}12H_2O$.

materials, thus improving the performance of cement slurry and satisfying the requirements of mine borehole sealing.[12,13]

This study analyzed two modified inorganic cement-based materials with PC and SAC as the base. First, the characteristics of their hydration products and their effects on their properties were analyzed. The status quo of studies on PC and SAC modified by additives such as coagulant regulators, admixtures, and nanomaterials was summarized. Finally, the effects of different additives on the properties such as hydration characteristics, coagulation time, and strength of cement-based materials and problems were discussed.

2. OVERVIEW OF BASIC PROPERTIES OF CEMENT-BASED MATERIALS

Inorganic materials, formulated by one inorganic substance alone or by many inorganic substances, can be divided into traditional inorganic materials and new inorganic materials. Modified cement-based materials, as improved materials based on traditional inorganic materials, are unique in their properties. Cement-based materials mainly fall into PC and SAC according to their main hydraulic substances, and the structure and properties of their hydration products are crucial to the properties of cement after hardening. Before reviewing and analyzing the modified cement-based sealing materials, it is necessary to grasp the chemical compositions and hydration products of cement-based materials. Table 1 lists the basic chemical compositions and hydration products of PC and SAC.

2.1. Analysis on the Performance of PC Hydration Products.

The PC clinker has the highest content of tricalcium silicate, and its main hydration products are about 70% C−H−S, 20% CH, and 10% AFt. Figure 1 shows the scanning electron microscopy image of the microstructure of PC hydration products. Massive fibrous C−S−H gel is crossed together; they serve as a cementing agent closely linking the dispersed cement particles and their hydration products. AFt crosses between C−S−H gel in a needle-shaped or columnar crystal structure, forming a skeletal support. CH is filled in the skeleton formed by C−S−H gel and AFt in a square or sheet structure, playing the role of sealing. According to the structure and properties of the above hydration products, it can be concluded that the strength of PC after hydration mainly depends on the hydrated C−S−H gel and AFt, and its sealing property comes from hydration products such as CH. The strength, coagulation time, and flowability of PC can be controlled to a certain extent by adjusting the hydration rates and quantities of hydration products such as C−S−H gel and AFt.

2.2. Analysis on the Performance of SAC Hydration Products.

SAC, which is the third-series cement invented in China in the 1970s, has the highest content of calcium sulfoaluminate in its clinker. Its hydration products are mainly classified into two types: hydrated calcium aluminates and gels. The former is mainly AFt (over 50%−60%) and AFm, while the latter is mainly C−S−H and AH_3.

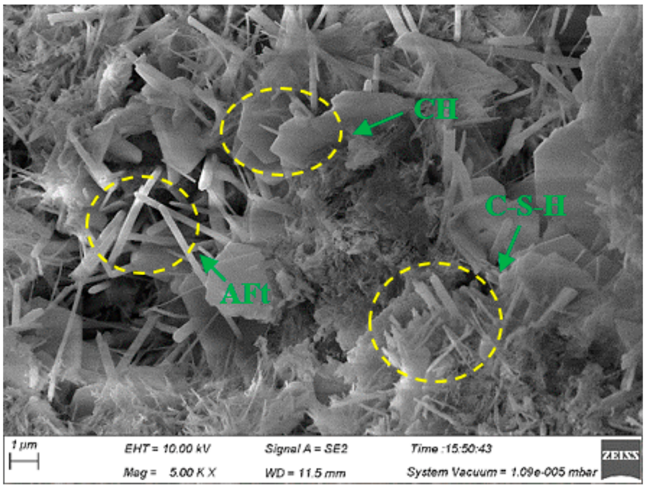


Figure 1. Microstructure of PC hydration products.

2.2.1. Effect of Hydrated AFt on SAC Performance. AFt, the most abundant substance in the SAC hydration products, controls the overall performance of SAC after hydration and hardening. The basic molecular unit of AFt, $\{Ca_3[Al(OH)_6]{\cdot}12H_2O\}^{3+}$, belongs to the tripartite crystal system and forms a needle-shaped or columnar crystal structure after hydration and hardening (Figure 2).[14] The molecular formula and molecular structure of AFt decide that its volume is prone to expansion. Studies have shown that the expansion depends on the PH value of slurry, i.e., the −OH concentration. The larger the PH value is, the more notable the volume expansion is.[14] Since AFt belongs to a high-strength tripartite crystal system, it can serve as the strength skeleton of gel-like hydration products and combine with them to form a tight "cement

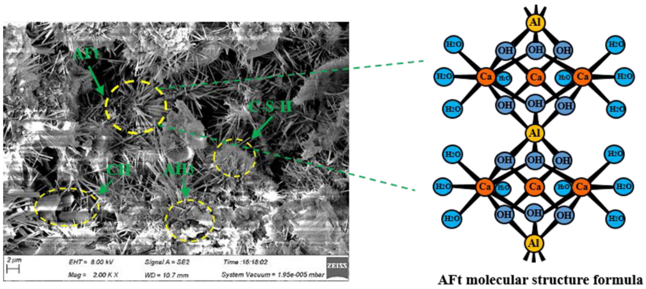


Figure 2. Microstructure of SAC hydration products and AFt molecular structure formula.

stone",[15] which endows SAC with a stable strength after hydration and hardening. Ca^{2+} concentration is the main factor for the formation and stabilization of AFt, and a higher Ca^{2+} concentration leads to the generation of more AFt, which contributes to the strength of SAC after hydration.[16]

2.2.2. Effect of Hydrated AFm on SAC Performance. Just like $Ca(OH)_2$ crystals, AFm also has a lamellar structure. Such a structure is characterized by sound thermal stability and anion interactivity. AFm can easily combine with anions in the external environment. When exposed to Cl^- in the external environment, AFm and Cl^- experience ion exchange to form AFm-Cl, which can protect the internal molecular structure of the cement base within a certain range. Therefore, AFm is equipped with strong chloride ion adsorption capacity and resistance to chloride corrosion.[17,18]

2.2.3. Effect of Hydrated Gel on SAC Performance. As the hydration time passes by, more AFt is generated, and the outwardly elongated crystal arms connect with each other to form a dense needle-shaped crystal spatial network structure.[19] Hydrated gels such as C−S−H and AH_3 fill the AFt spatial network structure, which leads to quick densification of cement stone. As a result, SAC coagulates rapidly and gains a high strength early. However, the generation of massive hydration gels raises the viscous force between cement particles and greatly reduces the fluidity of slurry.

Although both PC and SAC hydrate to produce C−H−S, AFt, CH, and AFm, their hydration properties differ remarkably, mainly due to the differences in the number of hydration products and the binding mode. As can be observed from the microstructure of SAC hydration products (Figure 2), AFt is generated in the largest quantity. The generated AFt provides a large number of connected dense pore skeletons in which other hydration products are filled to form a stable hydration product consolidation system. This stable system endows SAC with the characteristics of early and high strength, impermeability, and corrosion resistance.[20] Therefore, it is suitable for special projects such as low-temperature environment construction, emergency repair and construction, resistance to seawater corrosion, etc. PC hydration products have the highest C−H−S gel content. As a result, the connection between hydration products mainly relies on the interaction between C−H−S gels to connect, lacking pore skeletons, so PC is not as strong and tough as SAC after hardening. However, SAC also has defects such as difficulty in controlling coagulation time, slow strength development, easy shrinkage in the later stage, as well as poor compatibility with additives.[21] These problems, to a certain extent, limit the application of SAC in some special engineering environments.

3. MODIFIED CEMENT-BASED MATERIALS WITH PC AS THE BASE

3.1. Modification of PC by Admixtures. An admixture is the inorganic mineral fine powder added in the preparation of cement to improve the performance of fresh cement and hardened cement. It is as fine as or finer than cement. Common mineral admixtures include fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBS),[22] steel slag powder,[23] phosphorus slag (PS),[24] composite mineral admixtures,[25] etc. Only FA and SF are discussed here. Both FA and SF, as industrial waste, can be added to cement, as their addition not only reduces the cost of cement production but also improves the performance of cement paste and expands the application range of cement.

3.1.1. Effect of FA on PC Performance. FA, whose main chemical compositions are SiO_2, Al_2O_3, and Fe_2O_3, is fine ash collected from the fume of coal combustion and is the main waste material discharged from coal-fired power plants. FA, as an additive, can modify the coagulation and strength of PC-based materials. Niu et al.[26] contrastively analyzed the strengths and expansion rates of PC, PC+expander, and PC+FA and concluded that their strengths follow the order: PC+FA > PC > PC+expander. PC+FA is the hardest after solidification, and its expansion effect is superior to those of the other two materials. Their research proves the outstanding performance of FA in improving the solidification and expansion performance of PC. Tkaczewska[27] and Ding et al.[28] found that FA can decrease the compressive strength of PC by reducing the amount of hydrated C−S−H gel. By exploring the effect of FA admixture amount on the strength of PC, Ren et al.[29] disclosed that the early compressive strength of PC grows fastest when the FA admixture is 20%; however, as the maintenance time passes, an increasing amount of FA will suppress the growth of compressive strength. With respect to hydration reaction rate, scholars[27,30,31] found that FA can accelerate the hydration reaction of PC and shorten the coagulation time; FA makes C−S−H gel more densely connected and reduces coagulation shrinkage. The microstructure of FA in Figure 3 shows that FA is nanoscale particles, which can optimize performance mainly by filling the skeleton formed by PC hydration products. The faster the FA particles fill the skeleton, the more quickly the strength increases. However, excessive particles may cause swelling of the skeleton, thus decreasing the strength.

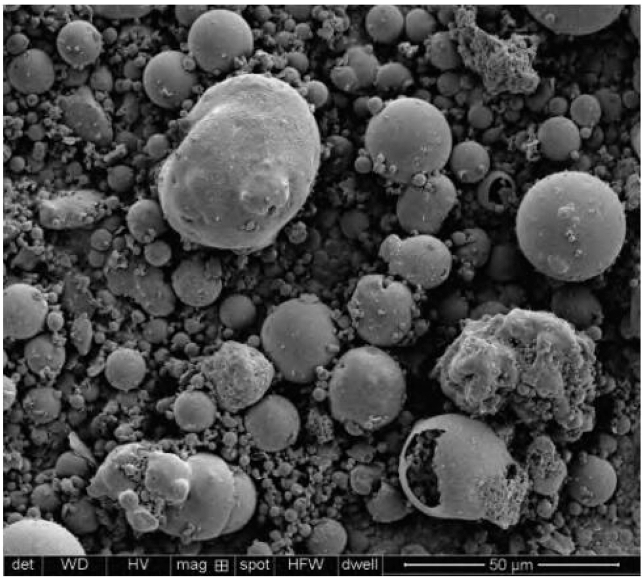


Figure 3. Microstructure of FA. Reprinted with permission from ref 30. Copyright 2022 Bulletin of the Chinese Ceramic Society.

In summary, FA not only is cost-effective but also can be recycled as waste. Besides, it can well improve the early strength of PC, shorten coagulation time, and reduce coagulation shrinkage. Thus, it is suitable for the development and promotion of sealing materials for gas extraction boreholes in mines.

3.1.2. Effect of SF on PC Performance. The main chemical compositions of SF are SiO_2 (97%), Al_2O_3 (0.4%), and CaO

(0.3%). As its average particle size is almost at the nanometer level, it has a large specific surface area and is highly active. Therefore, SF has a remarkable nucleation and filling effect when added into PC.[32] In terms of flowability and strength, Feng et al.[33] investigated the effect of SF on PC performance and concluded that SF could promote PC hydration. Under a constant water−cement ratio, a growing amount of SF corresponds to a faster increase in PC slurry viscosity and thus a decrease in flowability. According to the experiments on the influence of SF content on PC strength in Figure 4,[33,34] a SF content of below 5% promotes the PC compressive strength; the strength reaches the maximum under a SF content of 5%; and a SF content of over 5% inhibits the strength. Wang[35] obtained the same conclusion by performing experiments on the reinforcing properties of SF on PC. He believed that a SF content of 1.5%−2% promotes the PC compressive strength the most significantly and that SF can raise the early strength of PC by accelerating the transformation of CH and H_2O in PC into C−S−H gel and speeding up the hydration reaction. Compared to PC, SF has a tinny particle size. Its addition into PC is equivalent to the presence of microparticles around PC particles, which not only speeds up the hydration reaction but also achieves an excellent filling effect.

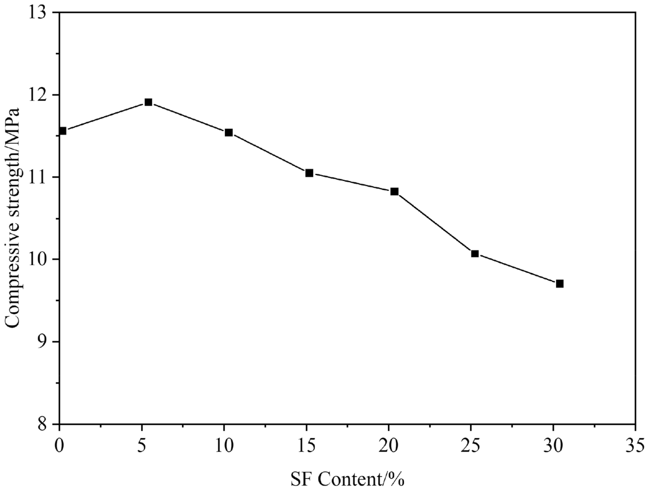


Figure 4. Effect of SF content on PC compressive strength. Reprinted with permission from ref 33. Copyright 2015 Applied Chemical Industry.

According to the above analysis, FA and SF share similarities in influencing the performance of PC. Both of them accelerate the hydration reaction of PC, improve the early strength, and shorten the coagulation time. In addition, as industrially generated wastes, FA and SF are both of low cost when serving as additives and can also be recycled as wastes. Their reasonable application to modify cement-based materials can not only improve their performance but also reduce the production cost and promote the development of green mining. Hence, they are suitable for the development and promotion of sealing materials for gas extraction boreholes in mines.

3.2. Modification of PC by Nanomaterials.

Recent years have seen the rapid development of nanotechnology, and nanomaterials are attracting considerable attention in modifying cement-based materials. The main nanomaterials are graphene (GP), graphene oxide (GO), and nano SiO_2.

3.2.1. Effect of GP on PC Performance. GP is the strongest material in the world, with a theoretical Young's modulus of up to 1.0 TPa, an intrinsic tensile strength of 130 GPa, and a fracture strength up to 42 N/m.[36] Due to its unique physical properties, it has received much attention and been used to improve the properties of cement-based materials. In terms of strength, Liu et al.[37] added GP into PC and concluded that GP has a significant effect on the strength of PC; the addition of 0.06% GP improves the compressive and flexural strength of PC by 10%. Bai et al.[38] concluded that the addition of 0.1%−2% GP leads to a decrease in the compressive strength, while the addition of 0.06%−0.1% GP notably increases the compressive strength. With respect to flowability, the research by Liu et al.[39] showed that GP reduces the flowability of PC slurry by raising its viscosity.

3.2.2. Effect of GO on the PC Performance. GO, an oxidation product of GP, shares the same physical properties as GP, but GO is more active because it contains more oxygen-containing functional groups. Qi et al.[40] investigated the dispersion ability of GO in PC hydrated pore fluid by absorbance, zeta potential, and atomic force microscopy (AFM) tests and found that cement-based slurry has the best dispersion effect under 0.03% GO, and its compressive strength increases by about 39.13% after solidification. Wang et al.[41] reviewed the effects of GP and GO on the properties of cement-based materials and concluded that GO significantly raises the strength of cementitious materials, especially cement-based materials. GP is inferior to GO in improving the strength; GO and GP influence the durability of cementitious materials mainly from three aspects, i.e., frost resistance, acid corrosion, and transmission properties. Qi[42] explored the effect of GO on the hydration properties of cement to further reveal its action mechanism, and he concluded that GO enhances the strength of cement-based materials in two ways: First, well-dispersed GO can accelerate the hydration process, providing many additional nucleation sites, raising the amount of hydration products and thus promoting the rapid crystallization and settlement of hydration products. Second, GO can influence the properties of C−S−H gel by filling the pores formed by C−S−H gel, thus increasing the compactness of C−S−H gel. Meanwhile, GO can form sound interfacial bonding with C−S−H to reduce the generation and development of microcracks, hereby improving the mechanical properties of cement-based materials.

The above studies all suggested that GP and GO can significantly improve the properties (such as strength and flowability) of PC. In fact, the special properties of nanomaterials cannot be truly exhibited unless they disperse excellently in the system. However, it is rather difficult to disperse GP completely in water because GP is only slightly soluble in water due to the lack of hydrophilic groups in its molecular structure. Excessive GP, which results in agglomeration,[43] not only fails to display its properties but also inhibits the performance of the dispersion system. Since the molecular structure of GO contains hydrophilic groups such as hydroxyl and carboxyl groups, GO boasts better dispersibility in water than GP. Therefore, the optimization of the performance of cement-based materials by GP and GO requires grasping the dispersion principle and method. Only in this way can adequate dispersion and a combination of GP and GO with hydration products be ensured, yet this is also the difficulty in current studies on the optimization of cement-based materials by GP and GO.

3.3. Effect of Combined Additives on the PC Performance. The above sections have introduced the effects of a single additive on the performance of PC. A single additive can only improve one or two performances rather than multiple performances at the same time. Currently, borehole sealing materials are expected to simultaneously achieve multiple performances, such as strong compressive strength, flowability, expansion property, and controllable coagulation time.

In improving the flowability, coagulation time, and expansion of cement-based materials, Zhao et al.[44] studied an inorganic slow-coagulation sealing material with bentonite and kaolin as the main materials and PC, FA, and sodium tripolyphosphate as auxiliary materials. Its physical properties include low water secretion, high permeability, and high suspension stability. Since slurry can remain unconsolidated for a long time, its large flow range enables it to diffuse well into fractures during borehole sealing. However, it has a low strength after solidification and tends to crack after being stressed; in addition, slurry can be easily lost via large fractures. Cao et al.[45] developed a modified cement-based sealing material with double-liquid grouting. Liquid A consists of bauxite and limestone, while Liquid B contains PC and alkaline oxide. Liquids A and B are both mixed with a certain amount of admixtures, such as water reducer, early strength agent, retarder, and accelerator. The results demonstrate that the ratio of sulfate to alkaline oxide in Liquid B is crucial to the compressive strength of the material. The variations of compressive strength (Figure 5) are obtained by exploring how different sulfate−alkaline oxide ratios influence the compressive strength of PC. According to Figure 5, under different water−cement ratios, the compressive strengths all reach the maximum at the sulfate−alkaline oxide ratio of 7. In addition, the flowability is the best when the water−ash ratio of the A and B mixture lies in the range of 0.8−1.

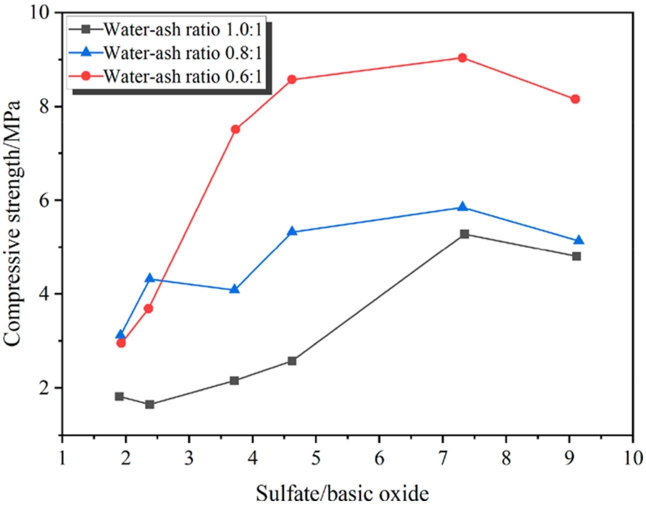


Figure 5. Effect of sulfate/alkaline oxides on the slurry strength. Reprinted with permission from ref 45. Copyright 2015 Coal Science & Technology Magazine.

Zuo et al.[46] developed an early strength cement-based borehole sealing material using the base materials of PC and SAC and the additives of bentonite, SF, expansion agent (a mixture of magnesium slag, FA, and sodium sulfate) and quick-coagulation earl-strength agent (a mixture of sodium carbonate, calcium hydroxide, and aluminum compound). The borehole sealing material coagulates initially within 60 min, and its compressive strength can reach 2.24 MPa in 1 day, 4.83 MPa in 3 days, and 7.05 MPa in 7 days. When the water−cement ratio is 1:1, the slurry has a high flowability and a low water secretion rate, which can meet the requirements of underground long-distance transportation. Meanwhile, the material boasts good microexpansion performance, and its sealing effect is superior to those of existing materials in coal mines. Li et al.[47] analyzed the performance of PC slurry by adding curing agents (CaO, SiO_2, Al_2O_3, and MgO), suspension agents (modified starch and fiber-based materials), bentonite (SiO_2 and Al_2O_3), and early strength agents (Na_2CO_3, NaOH, and Na_2SiO_3). Their study revealed that bentonite can change the slurry expansion and settlement stability; the suspension agent can decrease slurry water secretion; the early strength agent can quickly improve the early strength of the slurry; and the curing agent can significantly improve the later compressive strength of the slurry to 26%. Guo et al.[48] established an orthogonal experimental model between flowability and additives by the Desing−Expert software and investigated the effects of water reducer, water−cement ratio, retarder, and expander on the flowability performance of PC. The results indicated that the degrees of influences of additives on the fluidity of PC slurry follow the order: water reducer > water−cement ratio > retarder > expander. Besides, they prepared a new type of high-fluidity sealing material whose optimal experimental conditions are as follows: water reducer content of 0.5%, retarder content of 0.03%, water−cement ratio of 1, and expander content of 8%. Mesboua et al.[49] studied the performance characteristics of bentonite in cement-based mortar, and he concluded that bentonite combines with cement hydration products in a filling manner and can generate C−S−H gels; when bentonite is incorporated at 12%, the permeability resistance of cement-based mortar increases substantially. Zhang et al.[50] analyzed the mechanism of the effect of different additives on the hydration reaction of cementitious and reached the following conclusions: the reinforcing agent promotes the hydration of C_3S and C_2S minerals, generating a large number of C−S−H gels and $Ca(OH)_2$ crystals to achieve the reinforcing effect; the reaction of aluminum powder in the expansion agent produces $Al(OH)_3$ gel and promotes the hydration of C_2S to produce $Ca(OH)_2$ crystals; the resulting gel and crystals gradually encapsulate the tiny bubbles produced by the hydration reaction, so that the solidification body shows an expansion effect; and the suspension agent fills in between the hydration products while absorbing a large amount of water, which can reduce the water secretion rate of the slurry.

The above studies reveal that adding multiple additives to cement-based materials at the same time can improve many properties, but the interactions among additives and the influences of additives on the hydration process of PC have rarely been studied. Consequently, the determination of additive ratio is blind and requires multiple blending tests, wasting resources and manpower. The modification of PC by simultaneously adding multiple additive combinations is summarized in Table 2.

4. MODIFIED CEMENT-BASED MATERIALS WITH SAC AS THE BASE

4.1. Modification of SAC by Admixtures. *4.4.1. FA.* Jiang et al.[51] researched the effect of FA on the coagulation

Table 2. Modification of PC by Various Additive Combinations

ref	Base material	Additive	Performance improvement	Shortcoming
44	Sodium bentonite, kaolin	PC, FA, sodium tripolyphosphate, etc.	• Low water secretion • High permeability • High suspension stability • High flow ability	• Low strength • Tendency to crack
45	PC, bauxite, limestone, alkaline oxide	Water reducer, early strength agent, retarder, compound accelerator, etc.	• Fast coagulation • Early strength • High fluidity	• Complex additive compositions • Have difficulty in determining the appropriate ratio
46	PC, SAC	Expansion agent (magnesium slag, FA, sodium sulfate), rapid coagulation, and early strength agent (sodium carbonate, calcium hydroxide, aluminum compound)	• Early strength • High flow ability • Good expansion • Low water secretion	• Easy shrinkage of strength at the later stage
47, 50	OP	Curing agent, suspending agent, bentonite, early strength agent	• Good flowability • Early strength • Good expansion • High strength in the later stage	• Uncontrollable coagulation time
48	OP	Water reducer, retarder, expansion agent	• High fluidity • Good expansion • Controllable coagulation time	• Low strength
49	OP	Bentonite	• Good impermeability • Low water secretion	• Uncontrollable coagulation time

time and compressive strength of SAC, and the results showed that FA shortens the coagulation time. When 40% FA is added, the initial and final coagulation times is shortened by 76 and 94 min, respectively. The compressive strength variations are obtained by measuring the compressive strength of SAC under different FA contents (Figure 6). Figure 6 shows that the compressive strength decreases more notably when FA is added, and the decrease is the most significant at a maintenance time of 28 days, which indicates that FA inhibits the development of compressive strength of SAC. Ma et al.[52] studied the effect of FA on the performance of SAC and came to the same conclusion that FA shortens the coagulation time by decreasing the compressive strength and inhibiting the drying shrinkage of cement. Through X-ray diffraction and scanning electron microscopy, Su et al.[53] and Zhuo et al.[54] found that the effect of FA on SAC properties mainly depends on AFt generation. FA decreases the compressive strength of SAC by inhibiting the rate and amount of Aft generation.

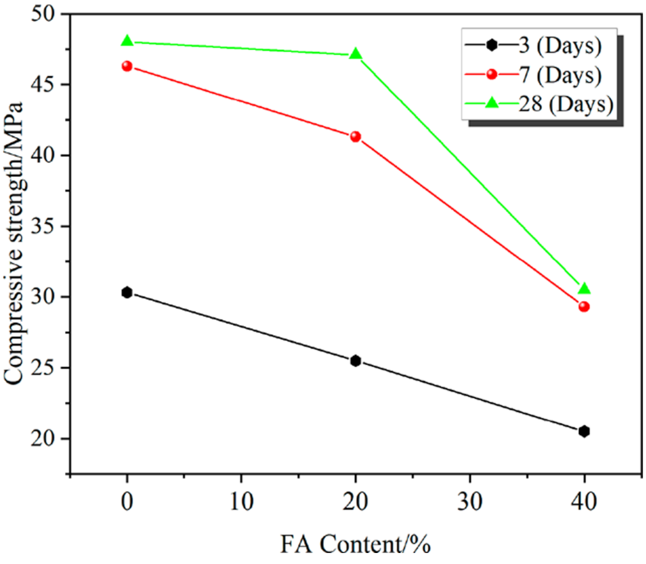


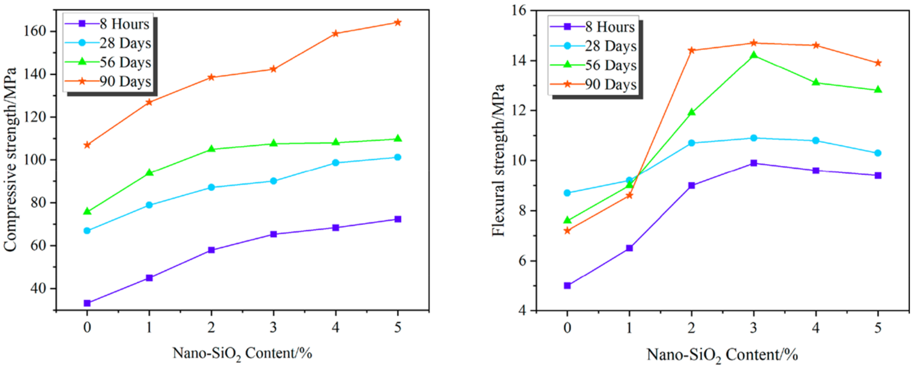
Figure 6. Effect of FA content on the PC compressive strength. Reproduced with permission from ref 51. Copyright 2016 Bulletin of the Chinese Ceramic Society.

4.1.2. SF. Liao et al.[55] explored the effect of SF on the hydration behavior of SAC and disclosed that the addition of SF significantly shortens the initial and final coagulation times of SAC slurry by 85 and 67 min, respectively. The reason is that SF particles facilitate nucleation of the hydration products, making them deposit on the surface of SF particles, which accelerates the crystallization of hydration products. As for compressive strength, the addition of 1%−5% SF promotes the strength of SAC, and the most significant improvement in strength is observed at 5%; a content of over 5% inhibits the comprehensive strength.[56,57]

In short, excessive FA and excessive SF both weaken the SAC strength by affecting the generation rate and quantity of hydration product AFt. Therefore, when modifying SAC by FA and SF, we should seriously consider the addition ratio for the purpose of improving the comprehensive performance of SAC.

4.2. Modification of SAC by Coagulant Regulators.

SAC coagulates too slowly in seepage prevention and borehole sealing projects, whereas it coagulates too fast in repair and grouting projects.[58] Therefore, reasonable application of coagulant regulators to SAC helps control the coagulation time and strength. Coagulant regulators can be classified into



(a) Compressive strength (b) Flexural strength

Figure 7. Effect of nano-SiO$_2$ on the mechanical properties of SAC. Reproduced with permission from ref 70. Copyright 2019 Bulletin of the Chinese Ceramic Society.

coagulants and retarders which can shorten and prolong the coagulation time, respectively.

4.2.1. Coagulants. Lithium compounds can serve as coagulants for SAC to accelerate its coagulation. Shen et al.[59] explored the effect of Li_2CO_3 on the hydration reaction of SAC. The results showed that Li_2CO_3 significantly accelerates the early hydration of SAC and shortens the coagulation time; besides, the coagulation time decreases with the increase in Li_2CO_3 amount. The initial and final coagulation times of SAC are shortened from 78 to 12 min and from 123 to 23 min, respectively, when the Li_2CO_3 amount is about 0.01%, proving the excellent coagulation promotion effect of Li_2CO_3.[59,60] Deng et al.[61] reached the following conclusions: three lithium compounds (Li_2CO_3, LiCl, and Li_2SO_4) can accelerate the SAC hydration reaction; in addition, the acceleration is primarily attributed to Li^+, while the other anions mainly affect AFt generation and exert a great influence on the strength. Wang et al.[62] explored how the three early coagulants, namely, FAS (mainly sulfate and silicate complexes), FAC (mainly sulfate and formate complexes), and CN (mainly anhydrous calcium sulfate), influence the performance of SAC. The following results were obtained: FAS, FAC, and CN all shorten the slurry coagulation time; moreover, aluminum sulfate and sodium silicate in FAS can improve the early strength of slurry by forming a dense spatial network structure through rapid generation of massive C−S−H gel and Aft. Calcium formate in FAC and anhydrous calcium thialuminate in CN accelerate the development of early strength of slurry by promoting AFt generation.

Therefore, lithium compounds are preferred to shorten the coagulation time of SAC, and a reasonable ratio of lithium compounds conduces to shortening the coagulation time of SAC and satisfying industrial requirements. In the meantime, FAS, FAC, and CN compound coagulants can be considered for simultaneously changing the early strength and coagulation time of SAC.

4.2.2. Retarders. Borax, sodium gluconate, and citric acid are common retarders. Generally, retarders inhibit the hydration reaction of cement by forming an encapsulation layer on the surface of cement particles.

Borax, chemically known as sodium borate ($Na_2B_4O_7$), is an inorganic compound. Its products include sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), sodium tetraborate pentahydrate ($Na_2B_4O_7 \cdot 5H_2O$), etc. In the study on the effect of borax on the hydration and hardening of SAC, it was found that borax exerts a slight retarding effect on SAC when its content is below 0.2%; the retarding effect is significantly enhanced when its content exceeds 0.3%; and the best performance is achieved under the borax content of 0.5%, with the initial and final coagulation times prolonged by 216 and 204 min, respectively.[63,64] In terms of strength, after the addition of borax, the compressive strength of SAC rises first and then declines with the passage of maintenance time, reaching the maximum under the borax content of 0.05%; it weakens when the borax content exceeds 0.05%.[65] Therefore, when borax is adopted to prolong the SAC coagulation time, an appropriate borax content is necessary for ensuring a certain compressive strength of SAC under the premise of a controllable coagulation time. Excessive borax would greatly lower the strength of cement slurry.

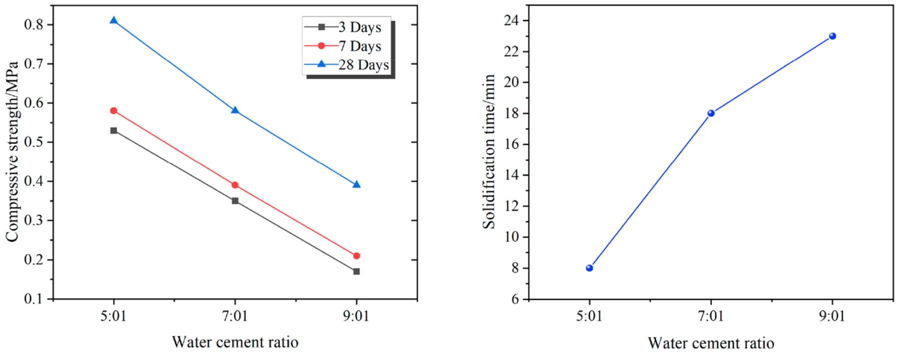
Sodium gluconate ($C_6H_{11}NaO_7$) can also effectively prolong the coagulation time of SAC. The retarding effect of sodium gluconate is the most significant under the content of 0.3%−0.6%, and the strength of SAC decreases when the content exceeds 0.6%.[66] Hu et al.[65] explained the mechanism of the retarding effect of citric acid on SAC as follows: calcium and citric acid form compounds in the SAC solution, and these compounds are adsorbed on the surface of SAC particles to prevent their hydration reaction. The retarding effect and strength of SAC are the most stable when the amount of added citric acid is 0.5%−0.6%. When the same amount of sodium gluconate and citric acid is added, the former can weaken the SAC strength more notably than the latter, and the former boasts a better retarding effect.

The retarding mechanisms of sodium citrate and sodium gluconate on SAC lie in that they are organic sodium salt retarders with certain surface activity. On one hand, they are adsorbed on the surface of cement particles to achieve the retarding effect. On the other hand, they combine with hydrogen bonds in water molecules through hydrophilic groups to form water film layers wrapped on the surface of cement particles, thus hindering the hydration reaction of cement and achieving the retarding effect.

4.3. Modification of SAC by Nanomaterials.

Studies on the modification of cement-based materials by nanomaterials mostly focused on PC, and there is a lack of relevant studies on SAC. Common nanomaterials for SAC modification include nano-SiO$_2$, nano-TiO$_2$, and nano-CaCO$_3$.

4.3.1. Nano-SiO$_2$. Abu et al.,[67] Ma et al.,[68,65] and Wang and Sun[69] investigated the effect of nano-SiO$_2$ on the mechanical



(a) Compressive strength (b) Solidification time and volume expansibility

Figure 8. Effects of different water cement ratios on the physical properties of super water-rich cement-based materials. Reproduced with permission from ref 75. Copyright 2021 Shandong Coal Science and Technology.

properties of SAC and concluded that nano-SiO_2 can improve the mechanical properties of SAC. They obtained the variations of compressive and flexural strengths (Figure 7) through tests on the mechanical properties of SAC with different nano-SiO_2 contents. According to Figure 7(a), the compressive strength of SAC slurry gradually is enhanced when the nano-SiO_2 content rises in the range of 0%−5%, and the compressive strength is promoted with the passage of SAC maintenance time under the same nano-SiO_2 content. This indicates that nano-SiO_2 can greatly influence the compressive strength of SAC at the later stage. As exhibited in Figure 7(b),[70] nano-SiO_2 influences the flexural strength of SAC the most significantly under the content of 3%, and the flexural strength is lower when the content is below or above 3%, which means that a reasonable amount of nano-SiO_2 is conducive to improving the toughness and crack propagation resistance of SAC.

Thanks to their large specific surface area, nano-SiO_2 particles can well adsorb water on the surface, thus weakening the flowability of slurry. The flowability of SAC decreases with the increase in nano-SiO_2 content, by 43% when the nano-SiO_2 content reaches 5%.[68] According to studies, nano-SiO_2 can well improve the mechanical strength of SAC, but it reduces the flowability of cement slurry.

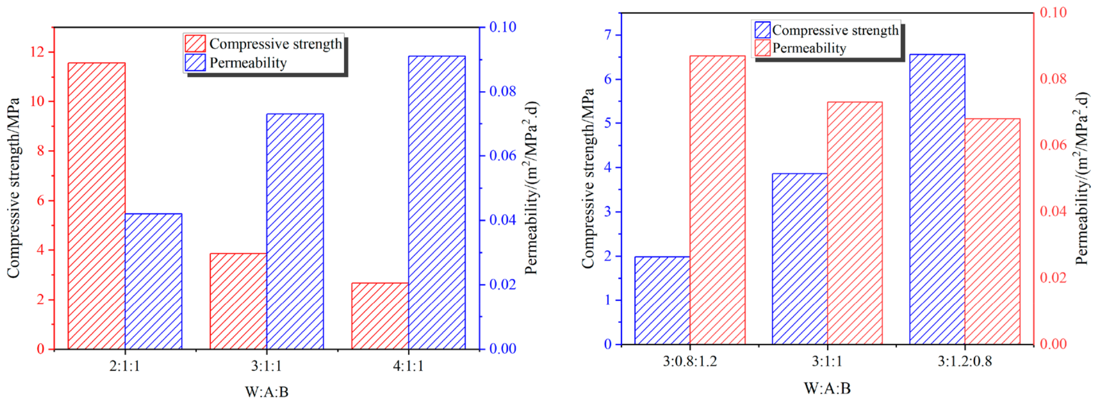
4.3.2. Nano-TiO_2 and Nano-$CaCO_3$. Nano-TiO_2 can accelerate the coagulation of SAC. The coagulation time is shortened the most obviously under a nano-TiO_2 content of 1%−5%; the highest compressive strength is observed when the TiO_2 amount is 2%.[71,72] Nano-TiO_2 can improve the SAC strength by accelerating the generation of SAC hydration products and raising the crystallinity of hydrated crystals. Nano-$CaCO_3$ and nano-TiO_2 influence SAC properties similarly. Nano-$CaCO_3$ can substantially improve the SAC strength by raising the crystallinity and generation rate of hydration product AFt, which leads to a monolithic uniform dense structure of the hardened SAC slurry.[73]

In summary, nanomaterials can densify the hardened cement by the nucleation and filling effect, thus improving the mechanical properties of cement. However, they may also greatly reduce the flowability of slurry. Therefore, the mechanical properties of cement should be comprehensively considered for determining the optimal content of nanomaterials.

4.4. SAC Water-Rich Materials. In deep mines and mines with complex terrain, often long-distance grouting is often adopted to seal boreholes on the extraction working face, which can reduce the transportation costs of grouting equipment and the hazards to operators. However, long-distance grouting has higher requirements for the performance of grout, and high water-rich cement-based materials are often used.[74] Currently prepared modified water-rich cement-based materials are highly flowable due to their high water−cement ratios. After various additives are added, they boast not only good flowability but also controllable coagulation time, low water secretion rate, superior expansion, and high mechanical strength. Hence, they have been widely used for sealing gas extraction boreholes. The properties of SAC make it a focus of studies on the preparation of modified water-rich cement-based materials.

Yang[75] tested the physical properties of super water-rich cement-based materials under different water−cement ratios (Figure 8). According to Figure 8(a), the compressive strength decreases significantly with the increase in water−cement ratio, indicating that the water−cement ratio is the main factor affecting the strength of water-rich cement-based materials. For sealing materials, a low compressive strength is unfavorable for sealing gas boreholes for the following reason: low-strength sealing materials crack easily under mining disturbance; as the fractures develop continuously in the extraction process, secondary or multiple grouting to seal boreholes is needed, which results in repeated construction. It can be seen in Figure 8(b) that the coagulation time is prolonged with the increase in water−cement ratio, which is also unfavorable for sealing gas boreholes by slurry because the slurry may seep from the fractures to the outside if it remains uncoagulated for a long time. Yang's experiments (2021) showed that substantially raising the water−cement ratio of cement-based materials alone is detrimental to the physical properties, as it can reduce the compressive strength and prolong the coagulation time. In view of this problem, scholars have modified the physical properties of super water-rich cement-based materials by experiments.

The compressive strength of SAC water-rich material is mainly controlled by the generation rate and amount of SAC hydration product AFt. Additives mainly change the compressive strength by affecting the amount of AFt.[76] Xu et al.[77] developed a double-liquid super water-rich filling material consisting of Liquids A and B with a water−cement ratio of 7:1. Material A was composed of coagulants and SAC, while Liquid B consisted of gypsum, lime, and retarders. The slurry



(a) Effect of water-cement ratio (b) Effect of material ratio

Figure 9. Effects of water–cement ratio and material ratio on compressive strength and permeability. Reproduced with permission from ref 78. Copyright 2021 Shandong Coal Science and Technology.

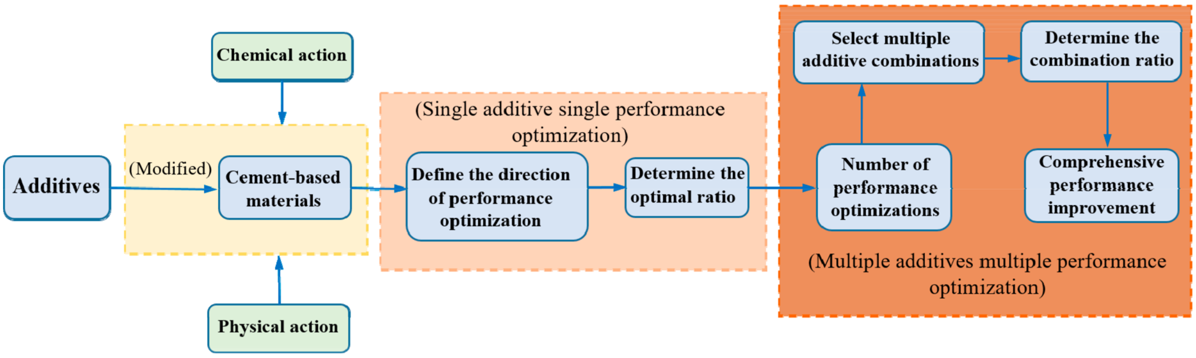


Figure 10. Flowchart of cement-based material modification.

formed by Liquids A or B alone could remain unconsolidated for a long time, yet their mixture formed a solidified body of certain strength quickly. Coagulants and retarders mainly controlled the coagulation time and flowability of slurry, while gypsum and lime controlled the strength of the solidified body. Li et al.[78] also studied a double-liquid water-rich sealing material consisting of Liquids A and B. Liquid A comprised SCA and retarders, while Liquid B was made of gypsum, lime, and coagulants. They researched the compressive strength and permeability of the materials at different water–cement ratios and material ratios (Figure 9 where W:A:B denotes the water–Liquid A–Liquid B ratio). It can be seen from Figure 9(a) that the compressive strength of the water-rich material decreases quickly with the increase in water–cement ratio when the material ratio remains unchanged. In addition, from Figure 9(b), as the material ratio increases, the compressive strength increases; yet, the permeability gradually decreases, which indicates that appropriate addition of additives such as gypsum, lime, or quick coagulant can well improve the strength and permeability of the water-rich material.

The above study shows that water-rich cement-based sealing materials are generally prepared with two liquids which can remain unsolidified alone for a long time. Once the two liquids are mixed together, they solidify in a short time, which explains why water-rich cement-based sealing materials can fulfill the requirement of long-distance grouting.

5. DISCUSSION

5.1. Modification Mechanism of Cement-Based Materials. The fundamental starting point for the modification of cement-based materials is to grasp their characteristics of chemical components and hydration products. Combined with the above analysis on the properties of PC and SAC hydration products, we can be sure that the hydration product properties play a decisive role in the physical properties exhibited by the materials after hydration and hardening. The generation process and structural changes of hydration products can be reasonably controlled in order to modify cement-based materials.

Additives modify cement-based materials from two aspects: chemical action and physical action. Chemically, additives affect the generation rate and quantity of hydration products by reacting with chemical components. Physically, additives affect the generation of hydration products or change the structure of hydration products through filling, adsorption, and nucleation. The properties of the following main hydration products should be grasped before studying the modification of cement-based materials: AFt controls the strength and volume expansion by forming a spatial skeleton; C–H–S gel controls the coagulation time and strength variation through cementing and solidification; fine gel hydration products such as CH and AH_3 control the flowability and compact the material by filling the skeleton of other hydration products; and AFm can improve the corrosion resistance by interacting with anions.

5.2. Modification Method for Cement-Based Materials. When various additives are combined to modify cement-based materials at the same time, a failure to grasp which performance they can optimize and their optimal ratios may cause blindness in selecting additives and determining ratios. It requires multiple blending tests, wasting massive resources and manpower. Therefore, the following studies should be done before modification. First, which performance the additives can optimize should be determined by analyzing their chemical and physical effects on cement-based materials. Second, the optimal ratio of a single additive in optimizing a single performance should be determined. Third, the ratio of multiple additive combinations should be determined according to the number of performances that need optimization so as to improve the overall performance. The flowchart of cement-based material modification is illustrated in Figure 10.

5.3. Modification Method for Water-Rich Cement-Based Materials. The excellent flowability of water-rich cement-based materials is beneficial for long-distance grouting, but they are unable to meet the performance requirements in actual grouting for their defects such as low strength, high water secretion rate, and long coagulation time. For water-rich materials, double liquids that can remain unsolidified alone for a long time rather than a single liquid are generally preferred in the hope of fulfilling the requirement of long-distance grouting. The main difficulties in modifying water-rich cement-based materials are as follows: (1) The slurry should secrete little water under a high water−cement ratio. (2) The slurry can solidify rapidly while maintaining high flowability. (3) The slurry has certain early strength after rapid solidification. Attention should be paid to two key points: first, each liquid should remain unsolidified for a long time when being stirred separately; second, the double-liquid mixture should solidify within the required time. The modification method is summarized as follows:

Step 1: to determine the water−cement ratio and coagulation time;

Step 2: to divide the additives into Liquid A and Liquid B according to which performance they can optimize. Liquid A contains additives that improve performances such as strength and expansion, while Liquid B contains additives that can control the coagulation time and the water secretion rate. Both Materials A and B contain a half water.

Step 3: to store and stir Liquids A and B separately and grout them together.

6. CONCLUSIONS

At present, studies on the modification of PC and SAC are still in the exploration stage. According to the research results in China, additives such as admixtures, coagulant regulators, and nanomaterials can improve the performances to a certain extent, and they have been applied in some practical projects. The review analysis and discussion are summarized as follows:

1. The modification of PC-based materials mainly focused on the improvement of strength, flowability, water secretion, and expansion. More attention was paid to the improvement of strength, while there is a lack of studies on the coagulation time and flowability. FA and SF exert a greater effect on the early strength, coagulation time, and shrinkage, and nanomaterials greatly influence the strength and flowability. The improvement of the performance of PC-based materials by combined additives requires a reasonable and optimized ratio.
2. The modification of SAC-based materials mainly focused on the improvement of strength, coagulation time, and flowability, with few studies on the improvement of expansion and water secretion. FA, SF, and nanomaterials influence the properties of SAC base and PC base in the same way; water-rich materials are mainly concentrated in the modification of SAC-based double-liquid materials.
3. The properties of hydration products of PC-based and SAC-based materials as well as their modification mechanisms and methods were analyzed and summarized.

Although the research on modified PC-based and SAC-based materials can provide theoretical guidance for the development of modified inorganic cement-based sealing materials for mines, there are still many problems. For example, coagulant regulators can hardly reasonably control the coagulation time; the activity of admixtures cannot be activated, leading to a reduction of cement strength; the nanomaterials decrease the cement slurry flowability; and the modification mechanisms of additives remain unclear. Therefore, taking advantage of outstanding aspects of each additive in performance modification and reasonably determining the optimal ratio of additives on the basis of grasping the modification mechanisms of additives are crucial for modifying inorganic cement-based materials (PC and SAC) and promoting their application in the borehole sealing practice.

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Notes

The authors declare no competing financial interest.

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