Research Progress of Advanced Cementitious Composites

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Abstract. This paper mainly introduces the definitions, properties, manufacturing methods of macro-defect-free cementitious composites, densified system containing homogeneously arranged ultra-fine particles, reactive power concrete, engineered cementitious composites, self-compacting concrete, their research situations at home and abroad as well as existing problems and solutions.

Keywords: Cementitious composites, Manufacturing, Microscopic Structure, Properties, Application.

1. Introduction
High-strength cementitious composites are an important part of cementitious composites. As more and more researchers have been committed to studying new cementitious composites in recent years. Some cementitious materials have been widely applied because of the development of advanced technologies and processes that can reduce the manufacturing costs. This paper mainly focuses on the current research situations of the following new cementitious functional composite materials.

2. Macro-Defect-Free Cementitious Composites
The macro-defect-free cementitious composites (hereinafter referred to as MDF) was invented by Professor Bitchall from Imperial Chemical Company Laboratory and Professor Howard from the University of Oxford in the early 1980s [1]. The manufacturing process of MDF (as shown in Figure 1) is to add a small amount of water, water-soluble polymers and glycerol into the cements, then to perform the compression moulding after high-efficiency shearing and mixing at a lower temperature. It is a kind of new cementitious material with a compressive strength of 200 MPa and a flexural strength of 60–70 MPa. On one hand, the improvement of the mechanical properties of this material is attributed to the elimination of macropores in the cement paste; on the other hand, this material is a kind of composite material of organic polymers and cements. The integration of organic matters and cementitious materials forms a spatial network structure and presents outstanding properties.
Subsequently, many researchers started to study MDF cementitious composites. At present, there are three main MDF composite systems, including calcium silicate cement/polyacrylamide (CSC/PAM), calcium aluminate cement/polyvinyl salcohol (CAC/PVA) and calcium chloraluminate cement/polyvinyl alcohol (CAS/PVA), but the CAC/PVA composite system has the best combined mechanical properties [3]. The compressive strength of MDF materials can reach 200MPa and the flexural strength can reach 300MPa. The Young’s modulus can reach 50GPa and the fracture toughness can reach $3\text{MPa} \cdot \text{m}^{1/2}$. It is easy to perform the mechanical treatment on materials with such a toughness value without brittle fracture [4, 5]. In addition to mechanical properties, the plasticity of MDF materials is also good before hardening so that they can be made into various complex shapes. Moreover, MDF materials have good dielectric properties, impact resistance, electromagnetic shielding effectiveness, acoustic properties, low-temperature performance and biological properties.

As the mechanical properties will be greatly reduced when MDF materials are in places with a high relative humidity or immersed in water, they have not been widely used. To develop the application of MDF cementitious composites, many researchers have used different processes to manufacture moisture-proof MDF cementitious composites in recent years. Normally, the humidity resistance of MDF cements is evaluated by placing the samples in a container with controllable humidity and measuring the samples regularly. Drabik et al. used different phases of humidity resistances in cements to mix sulphoaluminate-ferrite-dicalcium silicate with ordinary silicates to replace calcium aluminate cements so as to improve the humidity resistance [6]. In addition, they also enhanced the humidity resistance by changing the types and contents of water-soluble polymers. For example, in addition to polyphosphate sodium, hydroxypropyl methylcellulose, butyl acrylate and acrylonitrile, polyvinyl alcohol with different degrees of hydrolyzation and different average molecular weights can also be added. Titchell et al. removed the moisture-sensitive polymer phases through heat treatment at 500°C. Then heat-resistant polymers were added into the structure. Studies have proved the good humidity resistance of these materials. For example, when CAC-PVA cements are heated to 500°C and then undergo the rehydration process, the resulting new cements show zero loss of strength after being immersed in hot water at 20°C for 48 hours [7]. Lewis et al. reduced the chance of moisture to contact and penetrate a large number of polymers due to the impact on cross-linking agents. They used an organic cross-linking agent to increase the cross-linking degree of PVA. However, due to extensive
cross-linking, the process-ability of the pastes had been reduced before the manufacturing process was completed. So far, it is still unclear whether the addition of low cross-linking agents will achieve the desired effect [8]. Wang et al. used monomers and activators to replace polymers, aiming to have the in-situ polymerization during the hydration of MDF cements. The in-situ polymers of acrylamide monomers were mixed with sulphoaluminate and slags. The resulting MDF cementitious composites were immersed in water for four months while there was no significant decrease in the flexural strength. Although many measures have been adopted, they are all imperfect. The future direction of research on MDF materials should focus on the thorough improvement of the moisture sensitivity and deep applications [9].

3. Densified System Containing Homogeneously Arranged ultra-fine Particles
In 1981, Bache from the Alborg Portland Concrete Laboratory in Denmark first proposed the concept of densified system containing homogeneously arranged ultra-fine particles (hereinafter referred to as DSP) [10]. DSP materials are made of 70~80% of cements and 20~30% of silica fume (the particle size of 0.1~0.2μm), with 1~4% of superplasticizer and a small amount of water added at a water-cement ratio of 0.13~0.16. The manufactured compressive strength of the DSP material is 120~260MPa and the flexural strength is up to 150MPa. DSP materials are uniform high-density materials formed by chemical reactions between the particles with the closest compacting state through reasonable particle accumulation in accordance with the theoretical model of the closest packing based on the principle of particle science.

Later researchers incorporated ultra-fine fly ashes [11], slag powders and fibers on the basis of DSP materials. The compressive strength reached about 300MPa. The strengths of DSP materials were high. The compressive strength can reach 300MPa, the flexural strength can reach 150MPa. The elasticity modulus durability is also very good. The carbonization depth is zero. The strength loss after 300 freeze-thaw cycles is only 3%. The chloride diffusion coefficient is only about 10% of that of ordinary cements. It can be seen that the durability of DSP material is very good. Because DSP materials are very dense, the wear resistance is also very good. DSP materials have been widely used because of the high-strength, high durability, high wear-ability and good construction performance, including concrete protective layers under severe conditions, high-rise buildings and long-span bridges, corrosion-resistant ground and offshore platforms, bridge decks on busy roads, deicing salt roads in cold areas, and subways and other buildings requiring high durability. DSP materials are also ideal or nuclear power plants.

However, DSP materials also have some problems. The biggest problem is the brittleness. In recent years, some researchers have used methods such as adding a high proportion of superplasticizer and coupling agents to increase the toughness of DSP materials without reducing their strength. Huang Congyun et al. used CAS cementitious materials mixing with appropriate amount of modified materials such as silica fume, superplasticizer and coupling agent to manufacture high-strength DSP materials through special process measures. The compressive strength was 240MPa and the flexural strength was 140MPa [12]. Studies have shown that superplasticizer can not only improve the strength of DSP materials, but also greatly increase the toughness. In addition, the addition of coupling agents can increase the flexural strength of DSP materials from 83MPa to 137MPa with an increase of 39%. This is because the coupling agents have two different chemical functional groups, both organic and inorganic. In this case, the plasticizer can indirectly interact with CAS materials through the coupling agents, forming a strong interpenetrating boundary layer between the CAS materials and the superplasticizer, which is conducive to improving the strength and toughness of DSP materials [13].

4. Reactive Power Concrete
Reactive power concrete (hereinafter referred to as RPC) was developed in 1993 by Richard [14], an engineer from Bouygues, France. RPC materials are new cementitious materials with ultra-high-strength, ultra-high durability and ultra-high toughness. The name of reactive power concrete comes from the improved fineness and reactivity. The basic manufacturing principle of reactive power concrete is to remove coarse aggregate to improve the homogeneity; to enhance the compactness of the materials by
optimizing the particle gradation; to improve the micro-structure through thermal curing; and to increase the toughness by adding steel fibers. Reactive power concrete has good mechanical properties.

According to the compressive strength, reactive power concrete can be divided into two grades, RPC200 and RPC800. See Table 1 for mechanical properties. The fracture energy is shown in Figure 1. The manufacturing of RPC200 is to mix cements, micro silica, quartz sands and steel fibers evenly. First, add two-thirds of the superplasticizer-dissolved water for mixing, and finally add another third of the water to mix well. Pour the mixture into the mold for vibration molding and cure the mixture in the standard mode for 24 hours before releasing the mold. After that, cure the mixture in 90℃ water or steam. The manufacturing of RPC800 is similar to that of RPC200. Pressurize during molding to squeeze out excess water and then cure at a high temperature of 250-400℃ to hydrate the cements into hydrated calcium silicate gel. After that, dehydrate to form wollastonite crystals to improve the high strength.

| Concrete Type | HSC | RPC200 | RPC800 |
|---------------|-----|--------|--------|
| Pressurization During Condensation Period/MPa | None | None | 10~50 |
| Thermal Curing/℃ | None | 20~90 | 250~400 |
| Compressive strength/MPa | 60~100 | 170~230 | 500~800 |
| Flexural Strength/MPa | 6~10 | 30~60 | 45~140 |
| Fracture Energy/J·m⁻² | 140 | 20000~40000 | 12000~2000 |
| Elasticity Modulus/GPa | 30~40 | 50~60 | 60~75 |

In addition to excellent mechanical properties, RPC materials also have unparalleled durability [16]. The carbonization depth is zero, the concrete surface has no obvious damage performance after 1600 freeze-thaw cycles, the mass loss is almost zero, and the chloride permeability coefficient is 1/50 of ordinary concretes and 1/30 of high-performance concretes. The super durability is related to the good internal structure and the extremely low porosity. RPC materials had been widely used because of excellent mechanical properties and good durability. In July 1997, the pedestrian and bicycle bridge in Sherbrooke, Quebec, Canada was the first large-scale structure built with reactive power concrete in the world. The French Bouygues Company cooperated with the US Army Corps of Engineers to carry out the actual production of RPC products, including large-span prestressed concrete beams, sewage treatment filter panels, pressure pipelines and storage containers for radioactive solid wastes. RPC
materials have also been widely used in China. The sidewalk cover of the Fifth Ring Road in Beijing, the bridge cover of Zhengzhou-Xi’an high-speed railway and many sewages well covers are all made of RPC materials.

Although RPC materials have many advantages, they also have disadvantages. First, it is necessary to perform the heat treatment, which restricts the use. RPC materials can only be made into prefabricated parts and cannot be constructed on site. Secondly, the mechanical properties of RPC products manufactured by using different raw materials are also different. There is no uniform standard that can be used for reference. Thirdly, there are no unified structural design specifications for architectural designs. Only with structural design specifications can RPC materials be promoted and used. All these require a lot of efforts.

5. Engineered Cementitious Composites

The engineered cementitious composites (hereinafter referred to as ECC) were developed in 1992 in the Advanced Civil Engineering Materials Research Laboratory of the University of Michigan. Generally speaking, ECC materials are cements or cements with fillers, mixing with small particle fine aggregate as the matrix, and fibers as the reinforcement material. ECC materials are characterized by ultra-high toughness, high tensile strength and high fracture energy. The tensile strain value is greater than 3%, and the spacing of multiple cracking in the saturated state is less than 3mm [17]. The bending test in Figure 3 fully embodies the characteristics of multiple cracking and ultra-high toughness of the ECC materials. The strain hardening makes ECC materials have ultra-high toughness and fracture energy. In uniaxial tensile tests, ECC materials can produce multiple fine cracks from stress cracking to ultimate failure. In addition, the width of multiple cracking in the saturated state can be controlled within 100μm, which is 100-300 times that of ordinary concrete. The fracture energy is as high as 24kJ/m².

Relevant studies have shown that when the same tensile strain is generated, ECC materials and the concrete specimens present different cracking forms and widths. When the strain reaches 1.5%, ECC materials will produce fine cracks. The concrete specimen changes with the reinforcement ratio and the crack width varies from 0.15 to 25 mm. In the cracked state, ECC materials still maintain the permeability similar to that of the uncracked concrete, while the cracked concrete specimens present the disadvantages of poor water permeability and large crack width. As a durable building material required for infrastructure construction, the manufacturing cost of ECC materials is increased due to the strict requirements for raw materials and the complicated manufacturing process. However, with the in-depth research conducted by more researchers and the continuous development of high and new technologies, it is believed that ECC materials have broader application prospects than ordinary concrete in the near future.

6. Self-Compacting Concrete

The self-compacting concrete (hereinafter referred to as SCC) is a kind of concrete that does not require vibrations during pouring, which can be filled with densely reinforced templates only by dead weight and maintain its good homogeneity. This new type of concrete was developed by Professor Okamura from the University of Tokyo in the late 1980s. The self-compacting concrete uses superplasticizer and
active admixtures to improve the construction performance of concrete mixtures, so that the concrete can be compacted without vibrations. At the same time, the use of a large amount of mineral fine admixtures can reduce the concrete temperature and improve the resistance to carbonization so as to make the durability quite high. The raw materials of self-compacting concrete include cements, coarse and fine aggregates, active admixtures, superplasticizer, chemical tackifiers and water. Cements are required to be compatible with superplasticizer well. The C3A content and cements with low water consumption and standard consistency are more suitable for the manufacturing of self-compacting concrete. Generally, the content of C3A should be 8%. The gypsum used in the production of cements is preferably dihydrate gypsum, and the admixtures are preferably active admixtures. It is not suitable to use inactive admixtures. Fly ashes and coal gangue with a large burning vector are not suitable for the manufacturing of self-compacting concrete cements. The cements should be low-alkali cements. The coarse aggregates can be crushed stones or pebbles. Crushed stones can increase the strength, and pebbles can improve the fluidity of the concrete mixtures. Stones should be well-graded and well-shaped with a diameter less than 25mm. The fine aggregates should be washed sands with a fineness modulus of about 3.0. The sand rate is larger than that of ordinary concrete. The active admixtures can be blast furnace slag powders, fly ashes and silica fumes.

The self-compacting concrete has high fluidity, high stability and good abilities to pass through the gap between steel bars. The manufacturing principle of self-compacting concrete is to use the dispersion of superplasticizer to replace mechanical vibrations. During the manufacturing, through the accurate mixture and design of cementitious materials, coarse and fine aggregates, mineral admixtures, superplasticizer and other additives, the yield stress of the concrete mixture is small enough to be overcome by the shear stress generated by dead gravity, causing the concrete mixture to flow. At the same time, due to a certain number of active admixtures and chemical tackifiers, the concrete mixture has sufficient plastic viscosity, making the aggregates always suspended in the cement pastes without segregation and bleeding problems, thus ensuring the anti-segregation and bleeding of the concrete mixture and the passing ability of steel bars. They can flow freely and fully fill the space in the templates, thus forming a dense and uniform structure.

Although the self-compacting concrete is better than ordinary concrete in ensuring project quality and accelerating the construction progress, the self-compacting concrete will have volume shrinkage during the setting and hardening process. This shrinkage is the main cause of concrete cracks, which can directly decrease the concrete durability and even cause major accidents. Therefore, in recent years, researchers have conducted many studies about the improvement of fresh concrete performance and the reduction of the shrinkage. Li Zheng et al. studied the shrinkage compensation mechanism of expansion agents in the process of concrete hardening, and proposed the optimal combination of ternary composite gel materials composed of cements, fly ashes and expansion agents so as to obtain the optimal expansion performance and strength of concrete materials [19].

7. Other Cementitious Materials
In addition to the above-mentioned high-strength cementitious materials, high-strength cementitious materials that have emerged in recent decades mainly include alkaline-activated binder concrete (hereinafter referred to as ACC) and chemically bonded ceramic (hereinafter referred to as CBC). ACC materials are hardened bodied obtained through active mineral reactions of slags, fly ashes, metakaolin stimulated by alkaline substances such as sodium silicate and NaOH. The obtained hardened bodies form the silicon oxide tetrahedral chain through alkali. Therefore, the obtained materials have a strength of over 100MPa, which develops fast particularly at the early stage [20]. Gepolymer, popular in international research in recent years belongs to the alkali-activated binder concrete. However, the alkali-activated binder concrete has shortcomings of high brittleness and large shrinkage, restricting the wide application in the engineering field. CBC materials refer to cementitious materials whose properties are close to ceramics through chemical reactions at room temperature or lower temperatures (less than 400°C). Studies and applications of chemically bonded ceramics mostly focus on phosphate chemically bonded ceramics. Normally, CBC materials are cementitious materials with phosphates as
the binding phase generated through chemical reactions under acidic conditions based on the mixture of metal oxides, phosphoric acids or soluble phosphates, additives and mineral at a certain proportion. The phosphate chemically bonded ceramics will have chemical reactions at room temperature and then undergo condensation and hardening. The final hydrated product has high mechanical properties, high density, and resistances to acids, alkali and corrosion of ceramic products. It is a new type of cementitious material. The phosphate chemically bonded ceramics can be used to repair materials, cure harmful and radioactive wastes, and repair teeth and bones [21].

8. Conclusion
Cementitious composites have been the most widely used building materials in the world. With the development of advanced technologies and processes, cementitious composites are becoming high-strength, high-performance and multifunctional. The introduction of high-strength cementitious materials such as MDF, DSP, RPC, ECC and SCC has provided the manufacturing methods and ideas of high-strength cementitious materials, and summarized some rules and methodologies.

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