Optimization for Mix Proportion of Reactive Powder Concrete Containing Phosphorous Slag by Using Packing Model

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Abstract

A mix-design method based on packing model was used to optimize the mix proportion of Reactive Powder Concrete (RPC) containing phosphorous slag in this paper. The design aimed to achieve a densely compacted matrix by applying the modified Andreasen particle packing model, i.e., the Dinger-Funk particle size distribution (PSD) equation. MATLAB and Excel Solver Tool were utilized to implement the calculation of the design with four steps. The outcome of the design was quite similar to another two results obtained respectively through the method for minimum water demand of paste and through the orthogonal design for mix proportion of RPC. According to these three mix proportions, RPC specimens with volume fraction of steel fiber of 1% were produced after they had been cured in 95°C steam for 72 hours. Their compressive and flexural strength are more than 180 MPa and 28 MPa, respectively. Microstructural investigation of specimens through mercury intrusion porosimetry and scanning electron microscopy confirms the very low porosity and quite compact microstructure of the RPC.

1. Introduction

Reactive powder concrete (RPC) is a type of ultra-high performance concrete and is developed through micro-structural enhancement techniques, including the elimination of coarse aggregates, reducing the water-to-cementitious material ratio, lowering the CaO to SiO2 ratio by introducing the silica components, and the incorporation of steel micro-fibers (Chan and Chu 2004; Richard and Cheyrezy 1994, 1995; Wu 1999; Yazici et al. 2009). Nevertheless, the cement dosage of conventional RPC is generally high and silica fume (SF) content is often over 25% (by mass of the cement), which results in high materials cost, high energy consumption and embedded CO2 of RPC, and has negative effects on environmental protection. Replacing cement with mineral admixtures, including granulated blast furnace slag, fly ash, steel slag, rice husk ash, and decreasing SF content seemed to be a possible solution to these problems (Liu et al. 2003; Nguyen et al. 2011; Peng et al. 2010; Xiao et al. 2013; Yazici et al. 2008, 2009; Yiğiter et al. 2012). Previous studies suggested that incorporation of phosphorous slag powder (PS) in RPC was feasible (Peng et al. 2013, 2015).

The densest packing theory is considered as one of the basic principles for the production of RPC. It is commonly accepted that an optimal packing of granular ingredients is of crucial importance for achieving excellent mechanical strength and durability of cement-based materials (Borges et al. 2014; Brouwers and Radix 2005; de Larrard and Sedran 1994; Fétet 1892; Fuller and Thompson 1907; Hüskens and Brouwers 2008; Ng and Foster 2013; Peng 2009; Su et al. 2001). This can be achieved by optimizing the particle size distribution, and thus obtaining a much denser particle-packing of concrete ingredients (de Larrard 1989; Fétet 1892; Van-Tuan et al. 2011; Wu and Lian 1999; Yu et al. 2014, 2015). However, the packing properties of particles in RPC mixtures containing mineral admixtures have not been taken into account in the majority of current literature investigating the mix proportion design of the RPC. In most cases, the mix proportions have been given directly without any detailed explanation or theoretical support. In fact, incorporating fine mineral admixtures and optimizing the particle size distribution (PSD) of concrete ingredients both can improve the packing density of concrete, contributing to obtain RPC with high strength and excellent durability performance.

In studies regarding the particle-packing density of materials, scholars have proposed different mathematical models, which include the Furnas Model (Furnas 1928), Westman and Hugill Model (Westman and Hugill 1930) and its extension (Westman 1936), Aim and Goff Model (Aim and Goff 1968), modified Toufar Model (Goltermann et al. 1997), Dewar Model (Dewar 1999), Solid Suspension Model (de Larrard and Sedran 1994),
Table 1 Chemical composition and physical properties of cement, phosphorus slag powder, and silica fume.

| Items                      | Cement | Phosphorus slag (PS) | Silica fume (SF) |
|----------------------------|--------|----------------------|------------------|
| SiO₂                       | 21.05  | 38.84                | 96.90            |
| Al₂O₃                      | 5.11   | 3.46                 | 0.08             |
| Fe₂O₃                      | 2.90   | 1.40                 | 0.03             |
| Chemical composition (%)   |        |                      |                  |
| CaO                        | 61.46  | 46.09                | 0.12             |
| MgO                        | 1.34   | 1.83                 | 0.08             |
| SO₃                        | 3.64   | 1.34                 | 0.50             |
| P₂O₅                       | 0.18   | 2.45                 | 0.02             |
| Loss in ignition           | 2.36   | 0.24                 | 1.95             |
| Specific surface (m²/kg)   | 379    | 423                  | 20,000           |
| Density (kg/m³)            | 3100   | 2600                 | 2200             |
| Compressive strength (MPa)|        |                      |                  |
| 7 days                     | 42.7   | /                    | /                |
| 28 days                    | 53.5   | /                    | /                |

Linear Packing Density Model (de Larrard and Sedran 1994; Stovall et al. 1986), Compressive Packing Model (also named Compressible Packing Model) (de Larrard 1999; de Larrard and Sedran 1994) and Compaction-interaction Packing Model (Fennis et al. 2013). Each of these models can act as a useful tool for calculating the packing density of cementitious ingredients. They have been used already to investigate the packing properties of concrete mixtures consisting of coarse aggregate, fine aggregate and cementitious materials. Scholars have attempted to link the calculating results with performance of the concrete and to optimize the mix proportions based on the properties of granular materials (Amario et al. 2017; Borges et al. 2014; Brouwers and Radix 2005; de Larrard 1989; de Larrard and Sedran 1994, 2002; Fennis et al. 2013; Hüskens and Brouwers 2008; Vantan et al. 2011; Ng and Foster 2013; Peng 2009; Stovall et al. 1986; Su et al. 2001; Yu et al. 2014, 2015).

However, the above-mentioned models are not suitable to calculate the packing density of concrete mixture that generally consists of continuously graded ingredients. The reason is that these models are mainly based on the packing properties of binary or polydispersed particle mixes (Aim and Goff 1968; de Larrard 1999; de Larrard and Sedran 1994; Dewar 1999; Fennis et al. 2013; Furnas 1928; Goltermann et al. 1997; Stovall et al. 1986; Westman 1936; Westman and Hugill 1930), and that these models are using the packing of monosized particles to predict the packing of the concrete mixture made up of continuously sized particles. Thus, there is inevitably a quite large deviation between the theoretical and the actual results.

As for the packing properties of a continuously graded mixture, the fundamental works were carried out by Fuller and Thompson (1907) as well as Féret (1892) more than 110 years ago. Since then, a great deal of attempt has been done to solve the problem of grading of the particle mix, and the contributions of Furnas (1931), Andreasen and Andersen (1930), Dinger and Funk (1994), Brouwers (2005, 2006) and many others have been very helpful. Based on these fruitful works, this paper aims to achieve the following objectives using a packing model that deals with the packing properties of continuously graded size particle mixes:

1) To propose a mix proportion-design method based on the packing model, and to utilize the method to design the mix proportion of RPC containing PS;
2) To prove the applicability of the design method by method for the minimum water demand of cementitious paste and by orthogonal design of the mix proportion;
3) To gain RPCs with compressive strength of 180 MPa by utilizing the mix-design method; and
4) To investigate the microstructure of the RPCs through mercury intrusion porosimetry and scanning electron microscopy.

Materials and methods

2.1 Materials

The cement (C) used in this study is type PO 52.5 ordinary Portland cement (OPC) produced by Huaxin Cement Co. Ltd. (Yidu, Hubei Province, China). The granulated electric furnace phosphorus slag (PS) provided by Yichang Yatai Chemical Co., Ltd. (Hubei Province, China) was used as a filler to replace cement partially. The undensified silica fume (SF) provided by China Construction Ready Mixed Concrete Co. Ltd. was applied as reactive material, and its average particle size is 0.1 - 0.2 μm. A polycarboxylate-based superplasticizer provided by Jiangxi Building Materials Scientific Research and Design Institute (China) was used to adjust the workability of mixture. On the one hand, according to the microstructural enhancement techniques proposed by Richard and Cheyrezy (1994, 1995) for the development of RPC in 1990s, coarse aggregates were eliminated, replaced by fine sand (0.60 mm maximum), to enhance the homogeneity of the concrete. On the other hand, in order to ensure that the entire mix conforms to the densest possible packing theory, and to avoid the interference between fine aggregate and cement whose particle size is only second to that of fine aggregate, quartz sand with a size of 0.16 - 0.63 mm was selected as fine aggregate. The pertinent chemical and physical properties of the cement, PS, and SF are given in Table 1. The particle size distribution (PSD) curves of the materials are plotted in Fig. 1. Furthermore, brass-coated steel fiber with diameter of 0.2 mm...
was used to improve the ductility of concrete. The tensile strength and aspect ratio (length-to-diameter ratio) of steel fiber are 2800 MPa and 65, respectively.

2.2 Methodology of mix proportion design based on packing model

2.2.1 Proposal of the mix design method

For continuously graded mixture, there are many mathematical models that aimed to achieve the densest possible packing, such as the Fuller Model (Fuller and Thompson 1907), Andreasen Model (Andreasen and Andersen 1930) and the extension of the Furnas Model (Furnas 1931). Funk and Dinger modified the Andreasen model through the introduction of a limited small particle size in the powder, and the Dinger-Funk PSD equation was obtained (Funk and Dinger 1994):

\[
U(D_p) = 100 \frac{D_p^* - D_{min}^*}{D_{max}^* - D_{min}^*}
\]

where \(U(D_p)\) is a fraction of the total solids whose particles size are smaller than the sieve size \(D_p\), \(D_{min}\) and \(D_{max}\) are respectively the minimum and maximum particle size, and \(n\) is the distribution modulus which influences the ratio between coarse and fine particles in the total solids.

Through computing simulations and experimental research, Dinger and Brouwers thought that a continuous particle system can attain the optimal packing when the distribution modulus \(n\) is less than 0.37 (Brouwers 2005, 2006; Funk and Dinger 1994). According to the Dinger-Funk PSD equation, i.e., the modified Andreasen particle packing model, the PSD of a continuously graded mix can be obtained via the most compact theory. Among those mathematical models mentioned above, the Dinger-Funk PSD equation, which is based on the integral PSD approach of continuous grading mixes (Andreasen and Andersen 1930), shows conveniences by considering fine particles into design process (Borges et al. 2014; Brouwers and Radix 2005; Hunger 2010; Hüsken and Brouwers 2008; Ng and Foster 2013; Peng 2009; Yu et al. 2013, 2014, 2015).

It can be seen from the Dinger-Funk PSD equation that, the reduction of minimum particle size can also improve the packing and compactness of continuously graded mixture when the maximum particle size is constant (Brouwers 2005, 2006). This has been repeatedly confirmed by incorporation of fine admixtures in high performance and ultra-high performance concrete to increase the packing density of cement solids, thereby improving the performance of concrete. Brouwers and Radix (2005) pointed out that the PSDs of raw materials, including aggregates and cementitious materials, have a significant effect on the packing density of the mix. To attain a dense state, the PSDs of all granular solid materials must be taken into account to reduce the porosity of the granular mixture, hence gaining higher strength and workability. Based on the above research results, Hüsken et al. (2008) obtained self-compacting concrete (SCC) according to the Dinger-Funk PSD equation. The results show that, when raw materials with an appropriate PSD are matched in a proper proportion, high performance SCC can be attained with low cement content.

In this paper, the mix design of RPC containing phosphorus slag powder (PS) is based on the Dinger-Funk PSD equation. The proportions of each individual material in the mix, including cement, phosphorus slag powder, silica fume, and quartz sand, are adjusted until an optimum fit between the PSD of the composed mix and the Dinger-Funk PSD equation curve is reached.

Therefore, the PSD of the RPC solid mixture should comply with the Dinger-Funk PSD equation. Since the PSD of each involved material can be obtained by particle size analysis, the concrete mix design can be transformed into the following more general problem: the objective function (i.e., the Dinger-Funk PSD equation) is formulated using several known distribution functions (i.e., the PSD of each solid ingredient, including cement, phosphorus slag powder, silica fume, and quartz sand). When the fitting function matches or is quite close to the objective function, the matching ratio between the distribution functions is the result of the mix proportion design. Therefore, this design problem consists of three parts (Hüsken and Brouwers 2008; Peng 2009): (1) the target value or the objective function; (2) the regulation value or the adjusting function; and (3) restrictive conditions.

2.2.2 Target value

The solution of the mix design problem is that, the particle size distribution \(U_{mix}(D_i)\) of an aimed composition of concrete mixtures is required to meet the particle size distribution \(U_i(D_i)\) determined by the Dinger-Funk PSD equation, i.e., the particle size distribution \(U_{mix}(D_i)\) satisfies the following equation:

\[
U_{mix}(D_i) = U_{mix}(D_i) = 100 \frac{D_i^* - D_{min}^*}{D_{max}^* - D_{min}^*}
\]

where \(D_i\) represents the sieve size, \(U_{mix}(D_i)\) is the volume fraction of particles in concrete mixtures that are smaller than the sieve size \(D_i\), and \(U_{mix}(D_i)\) is the target particle size distribution. \(D_{min}, D_{max}\) and \(n\) are as same as
that in Equation (1).

Thus, the mix design problem involves the curve fitting of the particle size distribution \( U_{\text{mix}}(D_i) \) of the mixtures and the Dinger-Funk PSD equation curve. For this curve-fitting problem, it is required to minimize the deviation between \( U_{\text{mix}}(D_i) \) and the target curve \( U_{\text{tar}}(D_i) \) (i.e., Dinger-Funk PSD equation), which can be achieved by using the least squares method for its sum of the squares of the residuals (RSS) minimum (Hüsken and Brouwers 2008; Peng 2009), i.e.,

\[
\text{RSS} = \sum_{i=1}^{m} e_i^2 = \sum_{i=1}^{m} [U_{\text{mix}}(D_i) - U_{\text{tar}}(D_i)]^2 \rightarrow \min (3)
\]

This is the target value for the mix design problem. To assess the degree of fitting of the above curve-fitting problem, Equation (4) is introduced, where \( R^2 \) reflects the degree of deviation between the particle size distribution \( U_{\text{mix}}(D_i) \) and the target curve \( U_{\text{tar}}(D_i) \):

\[
R^2 = 1 - \frac{\sum_{i=1}^{m} [U_{\text{mix}}(D_i) - U_{\text{tar}}(D_i)]^2}{\sum_{i=1}^{m} [U_{\text{mix}}(D_i) - \bar{U}_{\text{mix}}]^2}
\]

where \( \bar{U}_{\text{mix}} = \frac{1}{m} \sum_{i=1}^{m} U_{\text{mix}}(D_i) \)

(4*)

2.2.3 Regulation value

The volume of each solid ingredient in per m\(^3\) fresh concrete is \( V_q \) (m\(^3\)) with \( k \) ranging from 1 to \( q \), where \( q \) denotes that there are \( q \) kinds of solid ingredients in concrete mixture. For ingredient \( k \), the cumulative percent finer than particles with diameter \( D_i \) (CPFT) is \( U_k(D_i) \), and the total volume of solid ingredients is \( V_S \) m\(^3\). The volume fraction \( v_k \) of ingredient \( k \) in the solid mixture and the CPFT of the solid mixture \( U_{\text{tar}}(D_i) \) are as in Equations (5) and (6).

\[
v_k = \frac{V_k}{\sum_{k=1}^{q} V_k} = \frac{V_q}{V_S} \quad (5)
\]

\[
U_{\text{mix}}(D_i) = \sum_{k=1}^{q} v_k \cdot U_k(D_i) \quad (6)
\]

Equations (5) and (6) are the regulated value or the adjusting function for the mix design problem. In addition, it should be pointed out that the total volume of solids per m\(^3\) fresh concrete is also changed by the optimization algorithm. The volumetric amount of solids per m\(^3\) fresh RPC is not directly connected with the target value. Thus, a connection exists via the restrictive conditions.

2.2.4 Restrictive conditions

Based on the given adjustable value and actual conditions, certain logistic and technical constraints should also be included.

Suppose that the volumes (m\(^3\)) of water and superplasticizer in per m\(^3\) fresh mixture are \( V_w \) and \( V_{sr} \), respectively. In addition, the fresh concrete contains a certain amount of air with volume (m\(^3\)) of \( V_{air} \). Then the restrictive conditions are as follows (Hüsken et al. 2008; Peng 2009):

(a) The volume and volume fraction of all kinds of raw materials are non-negative, i.e.,

\[
v_k \geq 0 \quad (k = 1, 2, \ldots) \quad (7)
\]

(b) Restrictive conditions of volume: The sum of the volume fraction \( v_k \) of solid ingredients is 1, and the sum of the total volume of all ingredients (including water, superplasticizer and air) in the fresh mixture is 1 m\(^3\), i.e.,

\[
\sum_{k=1}^{q} v_k = 1 \quad (9)
\]

(c) Technical restrictions: There is a certain constraint for the mix proportion parameters to ensure that the performance of concrete meets the design requirements. Typically, the limiting ratio parameters include minimum (or maximum) cement dosage, water consumption, minimum (or maximum) water-cement ratio and/or water-binder ratio, etc.

2.2.5 Implementation of program calculation

When the target value, the regulated value and the restrictive conditions have been determined and the PSD of each solid ingredient has been obtained, the mix proportion design problem can be solved by using MATLAB and Excel Solver Tool in Microsoft Excel.

2.3 Test methods

2.3.1 The minimum water demand of paste

The method for the minimum water demand of paste was proposed by Laboratoire Central des Ponts et Chaussées (LCPC) (de Larrard 1999) to determine packing density of powder, which is defined as the ratio of the total volume of all powder particles to the volume of space occupied by the powder, i.e., Equation (11):

\[
\Phi = \frac{V_{sp}}{V_S} \quad (11)
\]

where \( V_{sp} \) is the total volume of all powder particles, and \( V_S \) is the volume of space occupied by the powder.

This simple test requires only a balance (precision 0.1 g) and a conventional mortar mixer. The test method was as follows (de Larrard 1999; Peng et al. 2009). Taking a mass of 350 g of powder, which consisted of cement with or without mineral admixtures, the aim was to find the minimum water dosage that produced a thick paste. A slightly lower amount should give a humid powder. To blend the two products, the water was first
added in the mixer bowl, and then the powder. Mixed for 1 min at low speed followed by mixing for 1 min at high speed, scraped the bowl manually, and mixed again for another 5 min at high speed. After repeated tests, the minimum water demand \( (m_{w}) \) that just caused the mixture to change from a humid solid to a thick paste was obtained. Therefore, the packing density \( (\Phi) \) of mixture could be calculated as follows:

\[
\Phi = \frac{\sum m_i}{\sum \left( \frac{m_i}{\rho_i} \right) + \frac{m_w}{\rho_w}}
\]

(12)

where \( m_i \) and \( m_w \) are the respective masses \( (g) \) of cementitious material \( i \) and water \( w \), \( \rho_i \) is the density \( (g/cm^3) \) of water \( w \), and \( \rho_i \) is the density \( (g/cm^3) \) of cementitious material \( i \) as determined according to Chinese Standard GB/T 208-2014.

This method is based on the assumption that, the air content of fresh paste is neglected and the minimum water required just fills the interstices among all solid particles of the paste. Therefore, this volume of minimum water is equal to the volume of the interstices. It should be pointed out that although the minimum water demand \( (m_{w}) \) was obtained by the subjective judgment of the experimenter, the critical transition at which the mixture changed from solid to slurry (thick paste) do objectively exist. The purpose of the experiment is to find this transition point at which the amount of water added to mixture is the minimum after repeated tests (Peng et al. 2009). Actually, the minimum water demand of paste obtained by this method includes not only the interstitial water filling the interstices among particles but also the water adsorbed on particle surfaces, i.e., it is the maximum packing density that the paste mixture can achieve.

2.3.2 Measurement of fluidity of fresh mixture

The mix proportions of RPCs considered herein are these results of the mix-design method, of the orthogonal design experiment, and of the method for the minimum water demand of paste. For each mixture, all components (cement, PS, SF and quartz sand) were mixed, cast, and vibrated in a similar sequence as conventional concrete. Initially cementitious materials (cement, PS and SF) and quartz sand were mixed for about 3 min. The water and superplasticizer were then added and mixed for about 6 min. Subsequently, steel fibers were added (if necessary) and mixed for another 3 min. The entire mixing process took about 12 min. The fluidity of the fresh mixture was measured according to Chinese Standard GB 2419-2005 "Test Method for Fluidity of Cement Mortar".

2.3.3 Strength, scanning electron microscopy and mercury intrusion porosimetry

For measurement of strength (compressive and flexural) of RPC mixtures, prismatic specimens (40 mm × 40 mm × 160 mm) were cast. After the mixture had been mixed evenly, it was poured into the required molds, which had been sprayed with mold oil to reduce the friction at the interface between the molds and the mixture. The RPC mixture was compacted using a vibrating table. The cast molds were covered by plastic sheets before being demolded to prevent moisture in the mixture from evaporation. These specimens were demolded in 48 hours after casting due to the high PS content, which required longer setting time, and then were moved in a ZKY-400B Steam Curing Container for Concrete to be cured at 95°C for 72 hours. Finally, after the specimens had been cooled to room temperature in the Curing Container, they were placed in a water tank at 20°C until the age of 7 days. The strength was then tested according to Chinese Standard GB/T 17671-1999 "Method of Testing Cements - Determination of Strength".

For scanning electron microscopy (SEM) and mercury intrusion porosimetry, cubic specimens (40 mm × 40 mm × 40 mm) of each mixture were cast and prepared according to the above-described process. Samples were splinters taken from these cubic specimens and were oven-dried at 60°C for 24 hours. The SEM study was carried out by utilization of ULTRA PLUS scanning electron microscope at accelerating voltage of 20 kV. Porosimetric measurements were conducted on an AutoPore IV 9500 type porosimeter.

3. Results and discussion

3.1 Mix design of RPC containing phosphorous slag

3.1.1 Determination of the distribution modulus

Nowadays, the Dinger-Funk PSD equation has already been applied to optimize algorithms for the mix design of self-compacting concrete (Brouwers and Radix 2005), earth moist concrete (Hüskens and Brouwers 2008), ultra-high performance concrete (Peng 2009; Yu et al. 2014, 2015) and lightweight concrete (Yu et al. 2013). The distribution modulus \( (n) \) in the Dinger-Funk PSD equation determines the proportion between the fine and coarse particles in a mix. In general, higher values of the distribution modulus \( (n > 0.5) \) result in coarse mixture while lower values correspond to a rise in the proportion of fine materials in the mixture. Moreover, if \( n \) is less than 0.30, the mixture presents good workability while \( n \) less than 0.25 that means concrete mixes are rich in fine particles (Borges et al. 2014; Hüskens and Brouwers 2008). Thus, different types of concrete can be designed by using different values of the distribution modulus (Borges et al. 2014; Brouwers and Radix 2005; Hüskens and Brouwers 2008; Ng and Foster 2013; Peng 2009; Yu et al. 2014, 2015). Brouwers (2006) and Brouwers and Radix (2005) suggested that a theoretical \( n \) value range of 0 - 0.28 would result in an optimal packing. Hunger (2010) recommended using \( n \) in the range of 0.22 - 0.25 in the design of SCC. Therefore, considering that a high...
content of powder is required in RPC, the value of \( n \) is fixed at 0.25 in this study.

### 3.1.2 Determination of the restrictive conditions

Except for nonnegative conditions [Equations (7) and (8)] and volume constraints [Equations (9) and (10)], the restrictive conditions also include some technical constraints. For RPC, its cement consumption is very high, generally 400 - 900 kg/m³ and the content of silica fume is often over 25% of the cement mass. Moreover, previous studies (Peng et al. 2013; Sun et al. 2013) have demonstrated that the amount of water used in RPC containing phosphorus slag (PS) had better be less than 200 kg/m³ and the water-binder ratio could be less than 0.20, and phosphorus slag should be less than 40% of the mass of binder. Therefore, the technical restrictive conditions are:

\[
\begin{align*}
0.129 & \leq V_{\text{cement}} \leq 0.291 \\
0.001 & \leq V_{\text{PS}} \leq 0.20 \\
0.001 & \leq V_{\text{SF}} \leq 0.15 \\
0.015 & \leq V_{\text{W}} \leq 0.20
\end{align*}
\]  
(13)

### 3.1.3 The mix proportion of RPC

The optimum mix proportion of RPC containing PS was obtained by applying the design method, and the result is given in Table 2. The PSDs of all involved ingredients, the target curve and the grading line of RPC mix are shown in Fig. 2.

### Table 2 Optimum mix proportion of RPC obtained by applying the design method.

| Item               | Materials | Binders | Quartz sand | Water |
|--------------------|-----------|---------|-------------|-------|
| Volume \( V_k \) (m³) | SF        | PS      | Cement      | Water |
| Mass \( m_j \) (kg)  |           |         |             |       |
| Mass ratio\(^*\)     |           |         |             |       |

Note 1*: Taking the total mass of the binders as 1.

### 3.2 Verification of the mix proportion

#### 3.2.1 Result attained by using the method for the minimum water demand of paste

The effect of PS content (by mass of the binders) on minimum water demand and packing density of binary cementitious material paste (C + PS) is shown in Fig. 3. It can be seen from Fig. 3 that the minimum water demand of the binary cementitious material paste (C + PS) decreased with the increase of phosphorus slag (PS) content, and it was lowest when the content was about 35%. At this time, the volume fraction of interstices among the composite particles arrived at the minimum, and solid particles achieved the densest packing state. With further increase of PS, the minimum water demand rose and the packing density correspondingly decreased. Owing to the packing effect, PS particles filled the interstices among the cement particles, which improved the packing density of the (C + PS) system and reduced the filling water volume among the particles in the paste (Peng et al. 2009). In addition, as the specific surface area of the binary system rose, the amount of water in the surface layer of the powder particles enlarged, increasing the minimum water demand. Therefore, there is an optimal content of phosphorus slag to endow the binary mixture with a maximum packing density, which, in this research, is 35%, corresponding to a maximum packing density of the mixture of 0.650.

The effect of silica fume content (by mass of the binder) on minimum water demand and packing density of ternary cementitious materials (C + PS + SF) whose cement/PS ratio was kept at 0.65/0.35 were investigated. The results are given in Fig. 4.

As shown in Fig. 4, the effect of SF content on minimum water demand and packing density of ternary sys-
tem were similar to that of PS content on the properties of binary system. The minimum water demand of the ternary ingredients paste declined with the increase of SF content up to a limiting value of 15%. When the dosage of silica fume was 15%, the minimum water demand arrived at its minimum value, and the packing density reached its maximum of 0.673. When the content of SF further increased, the minimum water demand rose while the packing density decreased. This is because that SF particle are very small and can fill the interstices among the particle of cement and PS, diminishing the amount of water filled in the paste, thus further reducing the minimum water demand and correspondingly increasing the packing density of the ternary system. Similarly, there exists an optimal SF content (i.e., 15%) for the ternary system achieving a maximum packing density, which, in this research, is 0.673.

The above test results indicate that the optimal ratio of cement, PS and SF to obtain the maximum packing density is 55:30:15, which is quite close to the mix proportion of cementitious materials shown in Table 2, confirming that the mix-design method used herein is reasonable and feasible.

### 3.2.2 Orthogonal design for the mix proportion of RPC

The orthogonal design method was used to determine the mix proportion of RPC containing PS, and the factors and levels considered are shown in Table 3. The corresponding mixing proportions are displayed in Table 4. For each mixture, the content of superplasticizer and silica fume (SF) were 2% and 15% (by mass of the binder), respectively. The preparing process for RPC specimens is described above while the duration of steam-curing for each specimen is 48 hours. The strength of these specimens at 4-day age and the strength's range analysis are summarized in Table 4.

The result shown in Table 4 confirms that, among these factors, water-binder ratio (W/B) has the greatest effect on strength (flexural and compressive) of RPCs.

![Fig. 4 Effect of SF content on minimum water demand and packing density of ternary paste (C + PS + SF).](image)

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**Table 3 Factors and levels of orthogonal design for mix proportion of RPC.**

| Factor | PS (**) | W/B (**) | S/B * |
|--------|---------|----------|-------|
| ①      | 15%     | 0.16     | 0.6   |
| ②      | 25%     | 0.18     | 1.0   |
| ③      | 35%     | 0.20     | 1.4   |

**Notes**
1*: By mass of the binder, including cement, phosphorus slag (PS) and silica fume (SF).
2*: Including water from superplasticizer.

**Table 4 Mix proportions of RPC specimens and range analysis of their strength.**

| Mixture No. | PS (%) | W/B  | S/B  | \(f_{\text{f,4d}}\) (MPa) | \(f_{\text{c,4d}}\) (MPa) |
|-------------|--------|------|------|---------------------------|---------------------------|
| 1           | 15     | 0.16 | 0.6  | 16.5                      | 113.8                     |
| 2           | 15     | 0.18 | 1.0  | 17.5                      | 106.2                     |
| 3           | 15     | 0.20 | 1.4  | 14.4                      | 82.8                      |
| 4           | 25     | 0.16 | 2.0  | 18.8                      | 135.3                     |
| 5           | 25     | 0.18 | 1.4  | 19.4                      | 94.8                      |
| 6           | 25     | 0.20 | 1.4  | 14.7                      | 84.8                      |
| 7           | 35     | 0.16 | 3.0  | 22.9                      | 126.2                     |
| 8           | 35     | 0.18 | 1.4  | 16.7                      | 97.4                      |
| 9           | 35     | 0.20 | 1.4  | 14.1                      | 93.1                      |

**Range analysis of flexural strength at 4-day age \(f_{\text{f,4d}}\):**

|          | \(K_1\) | \(K_2\) | \(K_3\) |
|----------|---------|---------|---------|
| \(K_1\) | 48.4    | 58.2    | 47.9    |
| \(K_2\) | 52.9    | 53.6    | 50.4    |
| \(K_3\) | 56.3    | 43.2    | 56.7    |
| R        | 7.9     | 15.0    | 8.8     |

W/B has the greatest influence on \(f_{\text{f,4d}}\), and the influence of the S/B ratio and PS content is second. The smaller W/B, the higher \(f_{\text{f,4d}}\).

**Range analysis of compressive strength at 4-day age \(f_{\text{c,4d}}\):**

|          | \(K_1\) | \(K_2\) | \(K_3\) |
|----------|---------|---------|---------|
| \(K_1\) | 302.8   | 375.3   | 296.0   |
| \(K_2\) | 314.9   | 298.4   | 334.6   |
| \(K_3\) | 316.7   | 260.7   | 303.8   |
| R        | 13.9    | 114.6   | 38.6    |

W/B has the greatest influence on \(f_{\text{c,4d}}\), the S/B ratio is second, and PS content is last. The smaller W/B, the higher \(f_{\text{c,4d}}\).
The lower the W/B is, the higher the strength would be. The effect of both phosphorus slag (PS) content and sand-binder ratio (S/B) on strength of RPCs are not as great as that of W/B ratio. Based on the above findings, the optimum mix proportion of RPC was obtained, and is shown in Table 5.

It can be seen from Tables 2 and 5 that these two mix proportions of RPC are quite close, which verifies the feasibility of the mix-design method used in this study.

3.3 Properties of RPCs containing phosphorus slag

3.3.1 Fluidity of fresh RPC

Based on the mix proportions mentioned above, three batches of RPC composites were designed. Additionally, steel fiber was used to improve the ductility of concrete and to prevent explosive degrading under compression. For a conventional RPC, the fiber content is often more than 1 to 2% by volume of concrete, and sometimes reaches even 5% (Habel et al. 2006). In this study, the amount of brass coated steel fibers added to the RPC composites was 1%. The mix proportions of these six batches of RPCs are shown in Table 6.

The mixing process of each RPC mixture was the same one described in the second part of Section 2.3. The fluidity of fresh mixture was measured according to GB 2419-2005 and the results are given in Table 7.

As shown in Table 7, these three RPC mixtures without steel fibers, namely PS34-0, PS30-0, and PS35-0, possess a good fluidity. Mixture PS34-0 has the highest fluidity among these three mixtures. This is attributed to the densest packing of the mixture, which not only endows a quite low porosity of the hardened paste, but also has a higher paste-to-aggregate ratio resulting from the lower content of aggregate (see Table 6). Moreover, Table 7 also demonstrates the incorporation of steel fiber into RPC results in a slight reduction in the fluidity of fresh mixtures. This was due to the blocking effect of steel fiber. Even so, these RPCs containing steel fiber still owned sufficient workability for cast, which might derive from not only the short length as well as the low fraction of the steel fiber used, but also the dense packing of these mixtures.

3.3.2 Strength

For measurement of the strength of these RPCs, prismatic specimens (40 mm × 40 mm × 160 mm) were produced according to Table 6. The preparing process was described in Section 2.3. The strength was tested according to GB/T 17671-1999 and the results are tabulated in Table 7.

Table 7 suggested that the flexural and compressive strengths of these RPCs incorporating steel fibers are more than 28 MPa and 180 MPa, respectively, which are much higher than that of RPCs without steel fibers. It was thought that the excellent mechanical properties mainly result from the cracking resistance, enhancing and toughening effect of steel fiber in RPC (Peng 2009; Peng et al. 2011).

3.3.3 Scanning electron microscopy (SEM)

The microstructure of mixtures PS34-0, PS30-0 and PS35-0 was investigated by SEM, and the results are shown in Figs. 5, 6 and 7.
It can be seen from Figs. 5, 6 and 7 that the hardened paste of RPC specimens produced herein consists of a large number of hydration products, unhydrated particles, and a few pores. The unhydrated particles are tightly wrapped by hydration products, mainly calcium silicate hydrate gel, i.e., C-S-H gel [Figs. 5(a) and 7(b)]. These pores are filled by some crystal hydration products [Figs. 5(a), 6(c), and 7(b)] and gel products [Figs. 5(c), 6(c), and 7(c)], and the overwhelming majority of these pores are basically less than 5 μm. Moreover, the microstructure of the hardened paste is very compact. Actually, during the heat-curing process, the reactivity of cement, silica fume (SF) and phosphorus slag (PS) used in RPCs were further promoted, and the cementitious composites (C+SF+PS) hydrated sequentially (Peng et al. 2015), which continuously consumed portlandite produced by cement hydration and simultaneously produced more hydration products (C-S-H). These products filled in pores of the paste, decreasing porosity and enhancing microstructure of the RPC. Consequently, the hardened paste possessed a low porosity, which will be confirmed by investigation of mercury intrusion porosimetry (see next paragraph).

### 3.3.4 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry of selected RPC compositions, i.e., mixtures PS30-0, PS34-0 and PS35-0, was conducted using an AutoPore IV 9500 type porosimeter and the results are graphed in Fig. 8 and tabulated in Table 8.

As shown in Table 8, the porosities of these three RPC composites are close, ranging from 0.0298 ml/g to 0.0349 ml/g, and the diameter of the most probable pore is less than 5 nm. According to Wu and Lian (1999), the majority of the pores in these samples belong to the innocuous pores (diameter less than 20 nm) or the less harmful pores (diameter ranging from 20 nm to 100 nm), and the volume fraction of the harmful pores (diameter more than 100 nm) of mixture 34-0 do not exceed 35% (by the total volume of pore). These microstructure
characteristics give evidences of a low porosity of the RPC, which could benefit from 3 aspects: a high packing density of RPC mix, a very low water-binder ratio and the sequential hydration of the compound cementitious materials (Peng et al. 2009; Peng et al. 2015).

These microstructure characteristics revealed herein would definitely endow excellent mechanical and prominent durability properties of the RPC specimens. Nevertheless, the cracking resistance, enhancing and toughening effect of steel fibers could not be neglected (Peng 2009; Peng et al. 2011). Moreover, the effect of inclusion of steel fiber and interaction of agglomerating particles on the packing of RPC matrix has not been considered in this study and will be taken into account in the further investigation.

4. Conclusions

The mix proportion of RPC containing phosphorous slag (PS) was gained by using a mix-design method based on packing model, namely, the Dinger-Funk particle size distribution (PSD) equation. From the presented results, the following conclusions can be drawn:
(a) The design method is aimed to obtain a densely compacted concrete mixture by applying the Dinger-Funk PSD equation. The solution is determined through using MATLAB and Microsoft Excel, and there are four steps for it: (1) determining the value of the distribution modulus $n$ in the Dinger-Funk PSD equation; (2) selecting the target value and the adjustable value for the solution; (3) setting the restrictive condition of the mix proportion; and (4) optimizing the solution by adopting MATLAB and Microsoft Excel.

(b) The optimum mix proportion of RPC with phosphorus slag powder, i.e., the mass ratio of phosphorous slag powder, silica fume, cement, and quartz sand is 34:10:56:71, was obtained by using the mix-design method.

(c) The optimum mix proportion is quite similar to the results obtained respectively by the method for the minimum water demand of paste and by the orthogonal design for mix proportion of RPC.

(d) According to these mix proportions mentioned above, RPC specimens with steel fiber content of 1% (by volume fraction of the concrete) were produced after they had been cured in steam of 95°C for 72 hours. The compressive and flexural strengths of these specimens were more than 180 MPa and 28 MPa, respectively. Porosimetric investigation and scanning electron microscopy studies revealed the very low porosity and quite compact microstructure of the RPC produced herein.

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