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The effect of fly ash/slag on the property of reactive powder mortar designed by using Fuller's ideal curve and error function

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Abstract. This study is mainly focused on applying Fuller's ideal gradation curve to theoretically design blended ratio of all solid materials of a reactive powder mortar (RPM), also known as reactive powder concrete (RPC), with the aid of error function, and then to study the effect of fly ash/slag on the performance of RPM. The solid particle is assumed to be spherical particles. Then, the void volume of paste (*Vv*) and the paste content with specific quality can be obtained. As conclusion, under Fuller's ideal grading curve, the amount of fly ash/slag mixture is higher than that with silica fume along due to it better filled the void within solid particle and obtains higher packing density.

Keywords: reactive powder mortar (RPM); reactive powder concrete (RPC); Fuller's gradation curve; error function; fly ash/slag.

1. Introduction

Reactive powder mortar (RPM) or reactive powder concrete (RPC) is a generic name for a class of cementitious composite materials developed by the Richard and Cheyrezy in the early 1990s. RPC is also known as ultra-high-performance concrete (UHPC) that is characterized by excellent physical properties, particularly high compressive strength (200-800 Mpa) and flexure strength (40-50 Mpa) (Richard and Cheyrezy 1995, Matte, *et al.* 2000). Compared to high performance concrete (HPC), RPM is considerably more expensive to produce, but more isotropic nature and greater ductility make it competitive with steel. The typical mixture proportion of RPM includes large amount of Portland cement, extreme low *w/b* ratio by addition high dosages of latest generation superplasticizer (SP), the presence of high reactive pozzolan, and the incorporation of reinforced fibres. Conventional aggregate is completely replaced by a fine quartz or quartz flour with a particle size range between 150 and 425 μm (Feylessoufi, *et al.* 1996, Philippot, *et al.* 1998, Matte and

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Moranville 1998). Consequently, calling such composite material a "concrete" is somewhat of a misnomer and it more closely approximates a mortar. However, RPM is unique in attempting to optimize the entire grain size distribution of the composite matrix in order to reach maximum compaction (Chan and Chu 2004, Lee*, et al.* 2005). In Taiwan, the Hwang's research group tried to achieve the maximum dry loose density by simply packing all solid particles including coarse aggregates, sand and fly ash, to reduce the quantity of lubricating paste but keep desired workability for HPC (Hwang 2003, Chang, *et al.* 1995, Hwang, *et al.* 1996, Hwang and Jann 1998, Hwang Jann, 1998, Hwang and Chen 2002) as well as RPM. As the category of material is less than three, the blend ratio (α, β) (Hwang and Chen 2002, Lee and Hwang 2002) of solid materials can be easily obtained by experimental work, otherwise the packing seems difficult especially as the material size finer than μm. Therefore, it is necessary to adopt numerical approach to obtain proper packing order of all granular materials. Since the Fuller's gradation curve, on which the densification theory is based, has been successfully applied to asphalt concrete (AC), for concrete it has been only applied to blended coarse and fine aggregates but not been effectively applied to ultrafine particles as well as the particle category more than three (Mora, *et al.* 1998).

Here the Fuller's Curve is applied to enable fully packing with all solid particles such as sand, fly ash, slag and cement in size ranging from mm, μm to nm although it is not suggested to consider the size of particle finer than silica fume. To simplify the derivation, the aggregates are necessary to assumed to be spherical, which is definitely different from reality and thus will give rise to some errors. After determining solid particle ratio, the water content can be calculated based on the assigned amount of lubricated paste and quality of RPM.

2. Mixture design algorithm

2.1. Packing theory of solid particles

In 1909, Fuller and Thomson proposed the ideal curve as (Fuller and Thompson 1926):

$$\mathrm{P} = 100\,(d/\mathrm{D})^{h}\,;\ h = 1/3 \sim 1/2 \tag{1}$$

Where P : theoretical cumulative passing (%)
d : the individual sieve size; and
D : the maximum size of the particle.

By applying different h into Eq. (1), the result is plotted as Fig. 1 and it indicates the smaller the h the more the finer material and expected the more sticky of the paste.

2.2. Material

In this study type I Portland cement is used. Class F fly ash, BF Slag and Silica fume are from Taiwan Power Company, China Steel Corporation and Elken Company, respectively. The chemical analysis and specific gravity of the material is shown in Table 1 and the particle distribution of each material as well as comparable cement hydration product is shown in Fig. 2 where fly ash, cement, silica powder, slag and silica fume have some overlap and silica fume may fill some fine pores. The superplasticizer is Glenium 51 from Taiwan Durusle Company, Taiwan. The steel fiber, 13 mm in

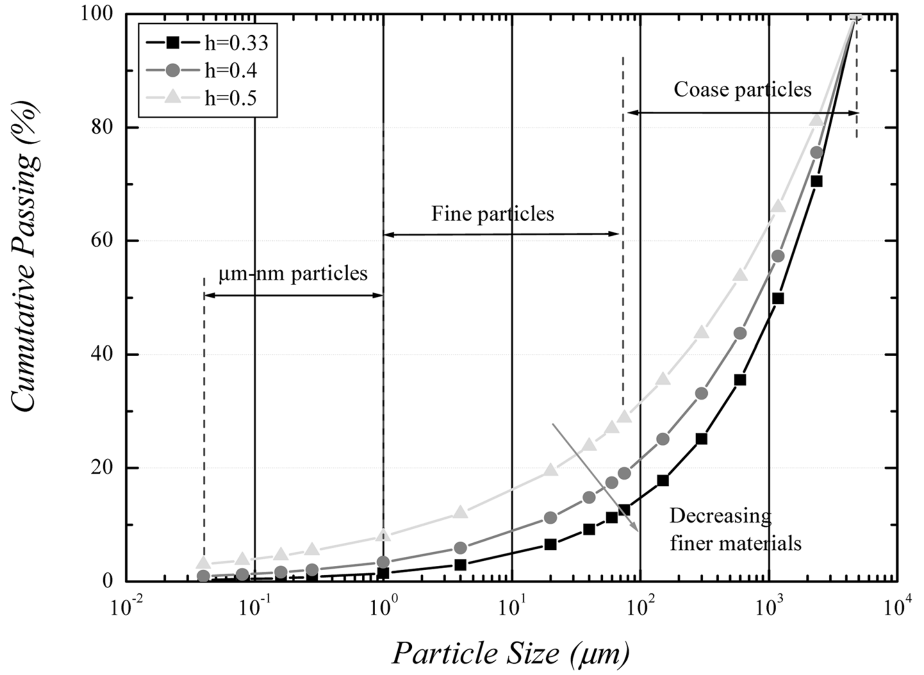


Fig. 1 The cumulative passing vs. particle size with different *h*

Table 1 Chemical analysis and physical properties of composite material

Items		Cement	Fly ash	Crushed quartz	Slag	Silica fume
Chemical	SiO_2	22.0	60.58	96.84	55.17	84.04
	Al_2O_3	5.6	18.54	0.13	11.13	0.43
	Fe_2O_3	3.4	11.39	--	0.6	0.71
	CaO	62.8	5.24	--	7.6	2.01
	MgO	2.6	1.67	--	0.24	2.87
	Na_2O	0.4	0.51	--	1.0	0.74
	K_2O	0.8	1.23	--	--	6.26
	SO_3	2.1	0.58	--	--	–
	P_2O_3	--		--	--	1.93
	L.O.I.	0.5	4.9	4.7	0.3	1.0
Physical property	Specific gravity	3.15	2.17	2.68	2.85	2.2

length and 0.25 mm diameter, is from Thurlen Company, Taiwan.

3. Results and discussions

This study mainly is focused on the theoretic approach of densified mix design algorithm combining with Fuller's grading curve to tailor design RPM mixture and further to optimize it. It starts to determine the blended ratio of each solid material via Fuller curve with error function, and

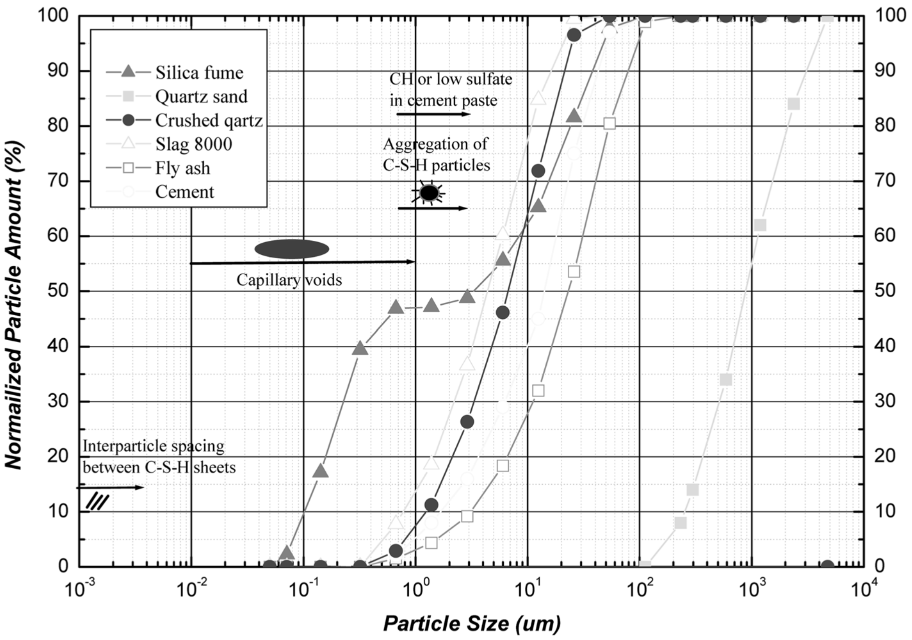


Fig. 2 The particle size distribution of each material of RPM and hydration products

then calculates the cumulated surface area, *S*, of each material on the basis of the blended ratio and measured V_v. By varing coating paste thickness, S_t, around solid particle the paste amount $V_p=V_v+S \cdot S_t$ could be estimated, and the "condition matrix" of the design criteria of safety and durability is finally used to calculate the mixture of RPM.

3.1. To establish the densified mixture model from Fuller's theory

Step 1: To estimate blending mixture of aggregates based on Fuller's grading curve according to Eq. (1), and applied an "error function" to optimize the proportion of each size material as to minimize the deviation by least square method as:

$$M = R^2 = \sum_{j=1}^{m}\left(\sum_{i=1}^{n} Pv_i a_{i,j} - k_j\right)^2 \tag{2}$$

where R is the error of the actually passing of *i*-material, $a_{i,j}$, deviates from ideal passing k_j by Eq. (1) through *j*-sieve.

After that, the optimal blended ratio $Pv_1 : Pv_2 \ldots\ldots : Pv_n$, (Example: $P_{\text{aggregate}} : P_{\text{fly ash}} : P_{\text{crushed quartz}} : P_{\text{silica fume}} : \ldots.$) can then be calculated.

The feature of Fuller's ideal gradation curve is depending on power (*h*), as shown in Fig. 3, and it indicates there is an optimum *h* between 0.33 and 0.5 that has highest unit weight of the mixture of sand, fly ash, crushed quartz and silica fume system. Such optimum point is corresponding to h = 0.4 where unit weight of blended mixture reaches 1155 kg/m^3 and the least void within solid particles (V_v) can be calculated.

Step 2: To calculate total surface area (*S*) of aggregates by statistics

The calculation of total surface area requires the aforementioned aggregate gradation data, as

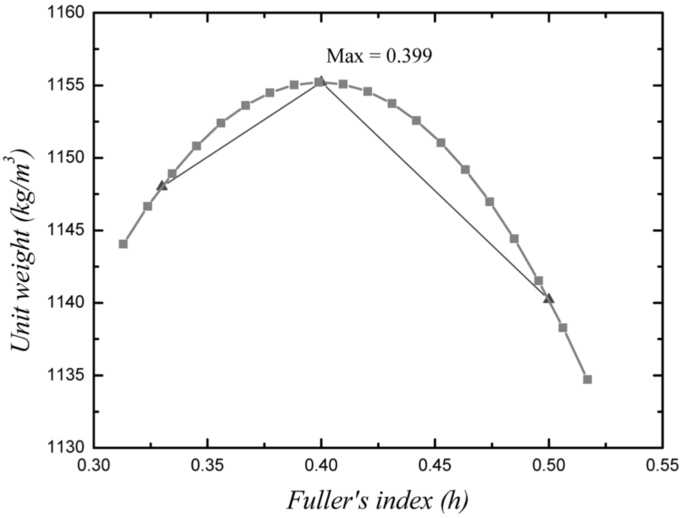


Fig. 3 The effect of *h* power of Fuller's curve on the unit weight of RPM mix

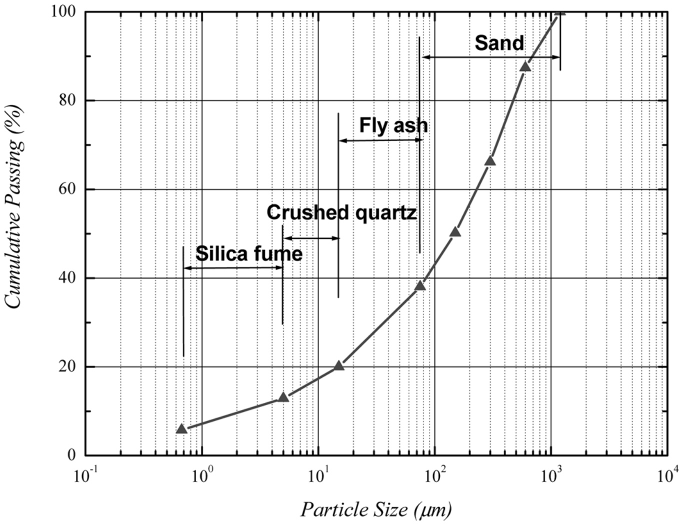


Fig. 4 The cumulative passing of RPM following Fuller's Curve

shown in Fig. 4, that obviously shows the size distribution of each solid particle, and needs

$$Kss_{,j} = \frac{6}{(\ln d_{i,j+1} - \ln d_{i,j})}\left(\frac{1}{d_{i,j}} - \frac{1}{d_{i,j+1}}\right)$$

to get the surface area of each individual aggregate size ranging between $d_{i,j+1}$ and $d_{i,j}$. Hence the entire surface area of blended aggregates (*Ksst*) including size finer than sand by using

$$Ksst = \sum_{j=1}^{4}\left[\left(\frac{p_1}{\gamma_1} a_j\right) Kss_{,j}\right] \tag{3}$$

Step 3: To assign a coating thickness of lubricating paste on particle

After assuming an arbitrary paste thickness (S_t), then one may apply the formula $V_p+V_v+S \cdot S_t$ and the blending ratio of each material as well as the void between aggregate to compute the required cement amount needed to fill the gap within aggregate (V_v) and to coat the particle surface (S).

Step 4: To compute the amount of each ingredient material

RPC mainly consists of seven materials, such as sand (w_{sand}), fly ash (w_{flyash}), crushed quartz (w_{powder}), cement (w_{cement}), BF slag (w_{slag}), silica fume ($w_{sliicafume}$) and water (w_{ater}). It is needed at least seven equations to calculate the mixture of ingredients, and three extra confining equations that concerns the safety and durability of mortar based on the existing knowledge of a healthy mortar. The amount of each material is derived via such condition matrix as follows:

$$\begin{bmatrix} w_{\#30} \\ w_{\#50} \\ w_{\#100} \\ w_{\#200} \\ w_{cement} \\ w_{flyash} \\ w_{powder} \\ w_{slag} \\ w_{silicafume} \\ w_{water} \end{bmatrix} = \begin{bmatrix} ksst\cdot S_t & ksst\cdot S_t & ksst\cdot S_t & ksst\cdot S_t & -\frac{1}{\gamma_{cement}} & -\frac{1}{\gamma_{flyash}} & -\frac{1}{\gamma_{powder}} & -\frac{1}{\gamma_{slag}} & -\frac{1}{\gamma_{silicafume}} & -\frac{1}{\gamma_{water}} \\ 1 & -\frac{Pw_{,1}}{Pw_{,2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & -\frac{Pw_{,1}}{Pw_{,3}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,4}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,5}} & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,6}} & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,7}} & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,8}} & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{Pw_{,1}}{Pw_{,9}} & 0 \\ 0 & 0 & 0 & 0 & \frac{w}{b} & \frac{w}{b} & \frac{w}{b} & \frac{w}{b} & \frac{w}{b} & -1 \end{bmatrix}^{-1} \times \begin{bmatrix} -V_v \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Table 2 RPC mix design by Fuller’s grading method (parts by mass)

Mixture method			Quartz sand #30	#50	#100	#200	Cement	Fly ash	Crushed quartz	Slag	Silica fume	Water	Fiber	*SP*	*W/C*	*W/b*
Fuller’s grading method	Assume cement is solid particle	1-1	244	240	235	235	291	199	248	262	202	119	--	50	0.580	0.14
				954												
		1-2	236	231	227	227	281	193	239	253	195	157	--	41	0.703	0.17
				921												
		1-3	228	224	220	219	272	186	231	244	189	196	--	28	0.826	0.20
				891												
		1-4	221	216	212	212	263	180	224	237	183	239		11	0.950	0.23
				861												
		1-5	221	216	212	212	224	180	224	237	183	185	234	33	0.825	0.20
				861												
	cement is not solid particle	2-1	146	143	140	140	861	120	148	121	156	244	--	38	0.327	0.20
				569												
Tradition(control))				900			720	-	205	-	250	204	--	40	0.339	0.20

Two basic varieties, deems cement material as solid particle or not, of RPM were design by Fuller’s ideal method. The mixture proportions developed for this study are in Table 2. Based on the same *w/b* ratio, say 0.2, the mix with cement considered as solid particle instead of binder has the least cement content, water content and the highest *w/c* ratio than others.

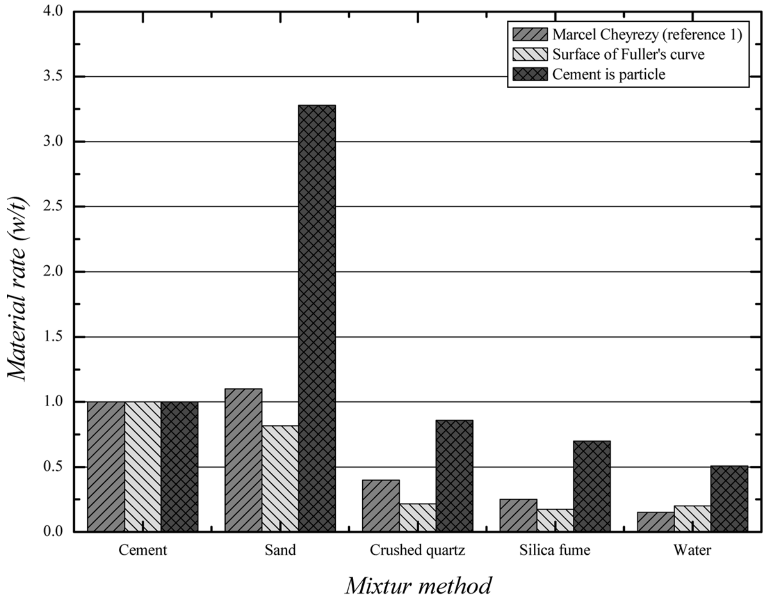


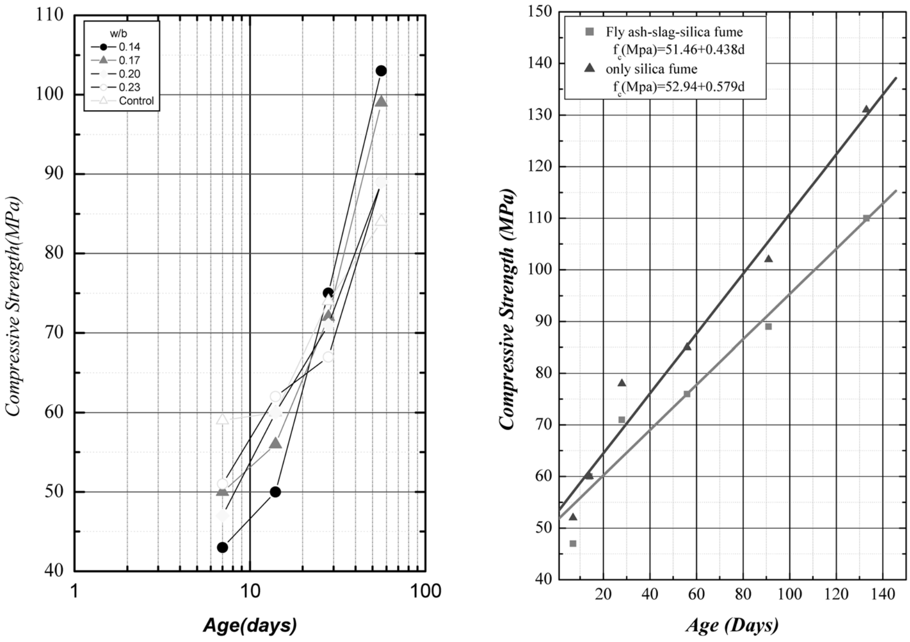
Fig. 5 The material ratio of RPM by different mix design algorithm

3.2. Effect of mixture method

The mixture proportion by using Fuller’s gradation analysis method obtained is showed in Fig. 5. The basic formula of Cheyrezy method is OPC cement: 1; Silica Fume: 0.25; Crushed quartz: 0.4; Sand: 1.1 (Richard and Cheyrezy 1995). If assume cement is not a solid material in the calculation by Fuller’s gradation method (Surface of Fuller’s curve), then the basic formula is cement: 1; silica fume: 0.175; crushed quartz: 0.215; sand: 0.817. If assume cement is a solid material in the calculation by Fuller’s gradation method (Cement is solid particle), then the basic formula is cement: 1; silica fume: 0.699; crushed quartz: 0.585; sand: 3.28. The results show that the amount of sand by Fuller’s ideal curve is about three times higher than that from Cheyrezy methods, and the ratio of crushed quartz/silica fume is the highest one. However if assume cement is not a solid in the calculation by Fuller’s gradation method, then the ratio of aggregate, crushed quartz and silica fume is the lowest one. As the quantity of cement is lowered, the total heat of hydration is expected to be low and the risk of thermal crack will hence be minimized.

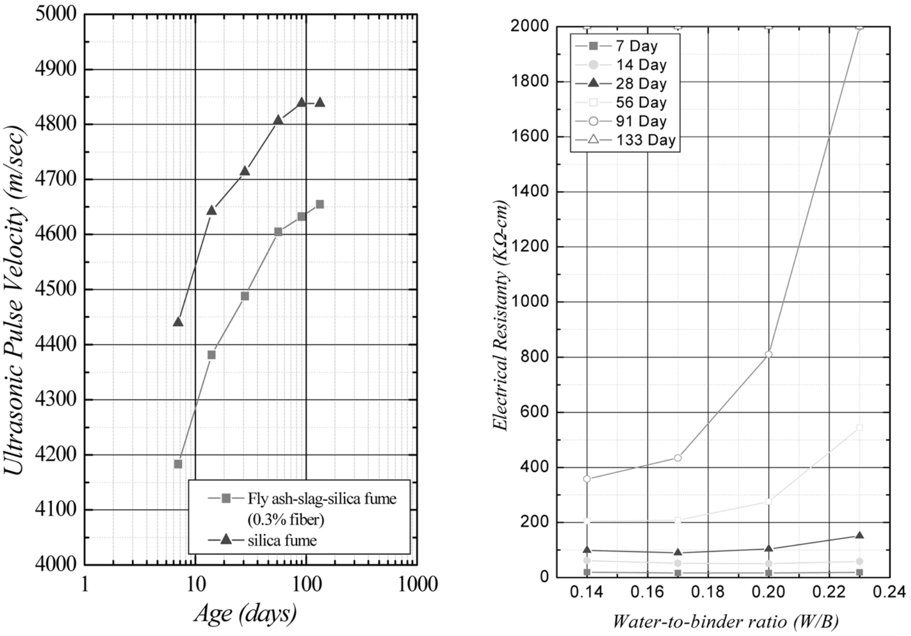
3.3. Effect of fly ash and BF slag on the property of RPM

As shown in Table 2, the addition both fly ash and BF slag to the RPM immediately shows a reduction in cement content and hence largely reduces the heat of hydration of RPM. According to the aforementioned mix designs with four types of pastes with *w/b*=0.14, 0.17, 0.20 and 0.23, and the corresponding compressive strength result is shown as Fig. 6(a). At early age, the compressive strength of control specimen, designated in Table 2 as tradition one, is higher than the aggregate-crushed quartz-fly ash-slag-cement-silica fume system by Fuller’s grading matrix due to high



(a) different w/b (b) different grading type

Fig. 6 The strength development of RPM with different *w/b* and grading type



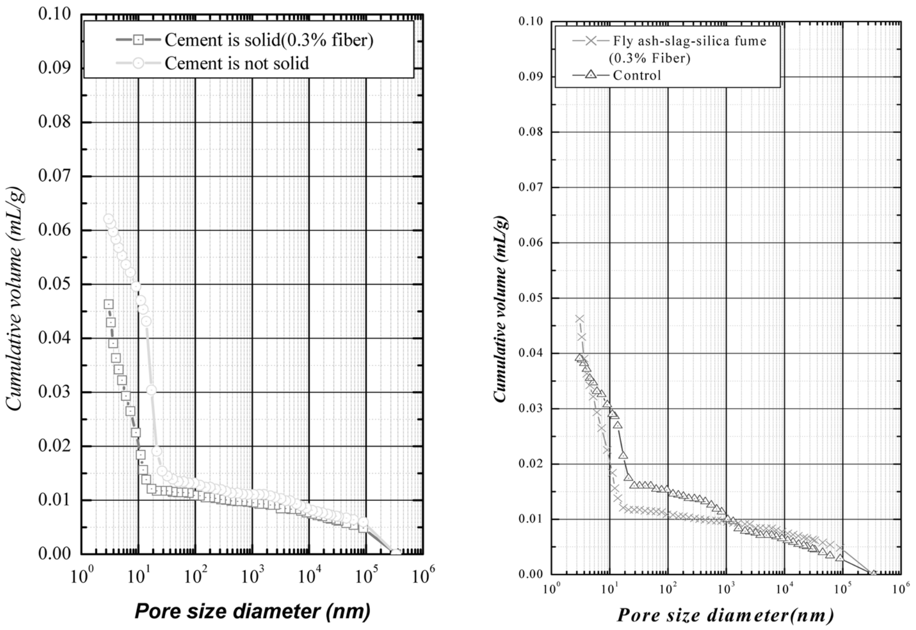
(a) (b)

Fig. 7 The ultrasonic pulse velocity and electrical resistivity for RPM

cement content, but at long-term the control is lower than others. Because water content and cement content are controlled as low as possible by Fuller's mixture design method, but the water keeps sufficient for pozzolanic material to react with alkali. Fig. 6(b) shows the compressive strength development rate of adding fly ash and BF slag is 0.438 MPa/day and is lower than that mixture with silica fume only (0.579 MPa/day). It means silica fume due to its particle distributed in more broaden could fill in void of solid particle and dense the structure, as shown in Fig. 2, and hence might activate the pozzolanic reaction.

The ultrasonic pulse velocity (UPV) with or without fly ash addition is shown in Fig. 7(a), and it indicates the UPV with the assumption of cement is deemed as a solid particle in calculation is higher than that cement is not deemed as solid particle. This further proves that silica fume may dense pack the solid particle as aforementioned. Hence the decreasing in cement paste content will eventually cause the increment in UPV of RPM The concrete resistivity is an important durability indicator for concrete structure according to AASHTO (Mora *et al.* 1998). Fig. 7(b) indicates that the resistivity is direct proportion to water-to-binder ratio (*w/b*) and increases with curing age. Since the concrete resistivity implies the difficulty of ion migration, the fomation gel via cement hydration and pozzolanic reaction tend to dense the pore structure and blocks the conduction path of electron. Therefore, the durability of RPM highly depends on the type of dense packing and water-to-binder ratio. However, this result also indicates that it may induce some autogeneous shrinkage crack due to lower w/c ratio than 0.42 that is supposed needed for complete hydration of tri-calcium silicate.

The pore size distribution of RPM by mercury-intrusion porosimeter (MIP) is shown in Fig. 8. The one with the addition of fly ash and BF slag tends to decrease total capillary porosity as well as decrease of cement content (as assume that cement deemed as solid particle) as shown in Fig. 8(a). Also the addition of fly ash and slag is effective on decreasing meso-pore ($50\sim10^3$ nm), but slightly



(a) (b)

Fig. 8 The pore size distribution of RPM with different mix

increasing the macro-pore (>10^3 nm) as shown in Fig. 8(b).

4. Conclusions

This study has found the following interesting points:

The application of Fullers ideal grading curve for mixture design is more efficient than conventional mixture design method and the application of the densified mixture design algorithm (DMDA) in laboratory especially as the category of particle (sand, crushed quartz, fly ash, BF slag and silica fume) is more than three (Hwang 2003).

Under Fuller's ideal grading curve, the dry loose density of mixture with the addition of fly ash and slag is higher than that with simple silica fume mixture. It is expected that the addition of fly ash and slag will filling the void within solid particle and achieve better packing density.

As consequence, the durability of RPC is improved depending on the packing type and water-to-binder ratio, and in such case it needs to decrease both cement and water contents.

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Notation

P	Fuller's curve passing, %.
D	Particle maximum size, mm.
$a_{i,j}$	j^{th} retained on the i^{th} particle.
p_{vi}	Particle volume percent on the i^{th} particle (%v).
γ_i	Bulk specific gravity on the i^{th} particle, kg/m^3
k_j	Ideal curve compute on the j^{th} percent retained.
$Kss_{,j}$	Surface constant on the i^{th} particle, 1/m
$Ksst$	Total the entire surface area, m^2/kg
S_t	Coating thickness of paste, μm
w_{sand}	aggregate per 1 m^3 of concrete, kg/m^3
w_{powder}	Crushed quartz per 1 m^3 of concrete, kg/m^3
w_{flyash}	Fly ash per 1 m^3 of concrete, kg/m^3
w_{slag}	Blast-furnace slag per 1 m^3 of concrete, kg/m^3
w_{cement}	Cement per 1 m^3 of concrete, kg/m^3
w_{SP}	Superplasticizer per 1 m^3 of concrete, kg/m^3

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