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Characterization of the granular packing and percolation threshold of reactive powder concrete

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Abstract

Reactive powder concrete (RPC) is a new cement-based material developed through microstructural engineering. RPC is composed of very fine powders: sand, crushed quartz and silica fume, all with particle sizes comprised between 300 and 0.02 μm, and a low water content, $W/C < 0.20$. A very dense matrix is achieved by optimizing the granular packing of these powders. This compactness confers to RPC ultrahigh strength and durability. The hydration kinetic of the cementitious matrix using electrical conductivity and isothermal calorimetry is presented. A linear relationship between the logarithm of conductivity $\ln(\sigma)$ and the degree of hydration α, has been found:

$$\ln(\sigma) = A_v - B_v \times \alpha$$

where A_v depends on the nature and the dosage of the different mineral and organic components, and B_v is an invariant related to the granular packing. From 19 different RPC compositions, an average value of 12.1 with a standard deviation of 1.7 were found for B_v. The capillary porosity percolation threshold was also deduced from this relationship. It has been found that when the degree of hydration is equal to 26%, the capillary pore space is discontinuous. This last result is in agreement with the prediction of the NIST microstructural model by Bentz and Garboczi [D., Bentz, E. Garboczi, Percolation of phases in a three-dimensional cement paste microstructural model, Cem Concr Res 21 (2) (1991) 325–344]. A continuous determination of the degree of hydration based on electrical conductivity is proposed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calorimetry; Degree of hydration; Electrical conductivity; Percolation theory; Reactive powder concrete

1. Introduction

Reactive powder concretes (RPCs) are characterized by a dense microstructure, obtained by the improvement of particle packing combined with a very low water content. The granular packing is improved using submicrometer particles that extend the particle size range, and results in an efficient filling of the packing porosity of cement grains.

The dispersing effect of a superplasticizer (SP) used at its optimal value decreases the water to cement ratio while improving the rheology of the paste.

This paper reports the influence of organic-based SP and mineral components on the pore connectivity deduced from hydration kinetic measurements using calorimetry and electrical conductivity. The C–S–H efficiency to fill capillary pores, the role of silica fume in the percolation process, and the percolation threshold are particularly investigated. All these data are compared to those predicted by the NIST microstructural model.

2. Materials

2.1. Reactive powder concrete

RPCs form a new generation of ultrahigh performance concretes [1]. In RPCs, the enhancement of the homogeneity is obtained by the elimination of coarse aggre-

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Table 1
Composition of RPC

Cement (kg/m^3)	Silica fume (kg/m^3)	Crushed quartz (kg/m^3)	Sand (kg/m^3)	Water (kg/m^3)	Superplasticizer (kg/m^3)
730	240	220	1040	150	Optimization

gates, the densification of the mixture results from the optimization of the grain size distribution, the improvement of the microstructure is achieved by post-set heat treatment, and finally a high ductility is obtained by the incorporation of steel fibers (2% in volume). In this work, fibers were not used because their presence could disturb electrical conductivity measurements. Moreover, it is supposed that fibers do not modify the granular packing of the paste because the diameter of the fibers, of about 0.20 mm, is close to the average size of the coarser aggregate (0.25 mm). The general composition of the studied RPC is given in Table 1.

The SP optimization step is explained in Section 2.4.

2.2. Cements

Four Portland cements were used in this study. Their characteristics are given in Table 2. These cements were selected for their wide compositional range. Their C_3A content, determined by quantitative XRD (internal standard), varies from 1% (Cem3, Cem4) up to 8% (Cem2). Their Blaine fineness ranges from 320 m^2/kg (Cem1) to 430 m^2/kg (Cem2). Their soluble alkali content is very low and is comprised between 0.16% (Cem1 to 3) and 0.38% (Cem4).

Except for Cem2, which is the most reactive of the four cements, these hydraulic binders are usually used to produce concretes having good workability: Cem1 is used currently to produce high-performance concrete, Cem3 is an oil well cement and Cem4 is a special cement having a very low heat of hydration and is used to build concrete dams. Cem4 is the cement that was used to build the footbridge erected in Sherbrooke [2].

2.3. Silica fumes

Three silica fumes (SF) were used in this work. Their industrial origin and their BET specific surface area are presented in Table 3. Their pozzolanic potential is measured through the quantity of reacted CaO during a Chapelle test (Table 3) [3].

SF1 and SF3 silica fumes are coproducts of the zirconium industry. Their specific surfaces are very close, respectively 12 and 11 m^2/g. SF2 is much finer (22 m^2/g). However, SF2 pozzolanicity is lower than that of SF1 and SF3, it combined only 442 mg/g of CaO in comparison to 665 mg/g and 616 mg/g, respectively, for SF1 and SF3.

The ions in solution given by silica fume particles were measured by inductively coupled plasma (ICP) with a water to solid ratio of one. Results for SF1 and SF2 are given in Table 4.

Table 4 shows clearly that SF2 contains more soluble impurities than SF1, 660 ppm against 69 ppm for the total amount of ions in solution.

2.4. Superplasticizers

Three types of polymers were studied : a copolymer of acrylic ester (CAE), a polynaphtalene sulfonate (PNS) and a polymelamine sulfonate (PMS).

These admixtures are synthetic polymers. CAE (SP1) contains carboxylic (COO^-) instead of sulfonic (SO_3^-) anionic groups present in PNS (SP2) and PMS (SP3) polymers. The molar ratio of anionic groups per organic monomer unit: acrylic group (CAE), naphtalene (PNS), melamine (PMS) is 1 for PNS and PMS, and is much lower than 1 for CAE copolymer [4].

To obtain a good workability and minimal secondary effects, the SP dosage was optimized with a rheometer, which is specially designed for RPC. The results of this optimization are given in Table 5 [5]. The dosage is expressed as the mass percentage of the solids of the SP related to the mass of cement used.

2.5. Studied RPC mixtures

Nineteen RPC mixtures have been made using the previously described materials : four Portland cements, three silica fumes, three SPs at four different dosages (optimum,

Table 2
Cements characteristics

Cement	C_3A (%)	Blaine fineness (m^2/kg)	Soluble alkali (Na_2O_{equi}.%)
Cem1	4	320	0.16
Cem2	8	430	0.16
Cem3	1	330	0.15
Cem4	1	360	0.38

Table 3
Silica fumes characteristics

Silica fume	BET specific surface (m^2/g)	Combined CaO (mg/g)	Origin
SF1	12	665	Zirconium
SF2	22	442	Silicon
SF3	11	616	Zirconium

Table 4
Ions in solution, W/SF = 1

Element (ppm)	Na	K	CaO	S	Mg	Al	P	Fe	Total
SF1	10	1	4	6	1	8	39	0	69
SF3	168	257	9	89	81	15	11	30	660

optimum −0.3%, optimum +0.3%, optimum +0.6%). The global composition of these mixtures is given in Table 5.

3. Hydration kinetics

The hydration kinetics of the cementitious matrix were studied using electrical conductivity and isothermal calorimetry. The initial reaction of the aluminates with water is not taken into account. Measurements began 20 min after the first contact of the water with the cement at 20C.

3.1. Electrical conductivity

In cement pastes, electrical conductivity is a function of the pore solution conductivity (σ_{sol}), the porosity (ϕ), and the dimensionless factor (β), which includes parameters such as pore connectivity and tortuosity, according to Eq. (1) [6].

$$\sigma = \sigma_{sol}\phi\beta \tag{1}$$

The pore solution conductivity σ_{sol} is the resultant of:

- different ions introduced in the mixing water (for example, admixture such as anionic-molecule-based SP and associated cationic counter-ion);
- dissolution of the mineral matrix;
- precipitation of different crystals or formation of organomineral compounds;
- variation of the pore solution volume.

3.2. Isothermal calorimetry

The degree of hydration can be reached through isothermal calorimetry. The integration of the thermal flux (Q) gives the hydration heat, which is proportional to the degree of reaction according to Eq. (2):

$$\alpha = \frac{\int_0^t Q\mathrm{d}t}{\int_0^\infty Q\mathrm{d}t} \tag{2}$$

The complete hydration heat $\int_0^\infty Q\mathrm{d}t$ is calculated with the enthalpy values for each clinker phase [7]. Data and results are given in Table 6.

High SP dosage in RPC could result in the formation of an organomineral compound rather than ettringite [8]. However, complete hydration enthalpy associated with ettringite is chosen; in this case, anionic organic molecules take the place of sulfate ions.

3.3. Measurements

The induction period ends when $Ca(OH)_2$ precipitates. This strong precipitation corresponds to the maximum of conductivity (σ_{max}) and a minimum of heat flux (Fig. 1).

Table 5
Composition of RPC studied

SP	RPC	Cement	SF	SP molecule	SP dosage (solid %)
Optimal dosage	RPC1	Cem1	SF1	CAE (SP1)	0.7
	RPC2	Cem2	SF1	CAE (SP1)	1.2
	RPC3	Cem3	SF1	CAE (SP1)	0.6
	RPC4	Cem4	SF1	CAE (SP1)	0.8
	RPC5	Cem1	SF2	CAE (SP1)	1.2
	RPC6	Cem1	SF3	CAE (SP1)	0.7
	RPC7	Cem1	SF1	PNS (SP2)	1.7
	RPC8	Cem1	SF1	PMS (SP3)	2.2
	RPC9	Cem2	SF1	PNS (SP2)	2.4
	RPC10	Cem1	SF2	PNS (SP2)	2.7
Optimal dosage −0.3%	RPC11	Cem1	SF1	CAE (SP1)	0.4
	RPC12	Cem1	SF1	PNS (SP2)	1.4
	RPC13	Cem1	SF1	PMS (SP3)	1.9
Optimal dosage +0.3%	RPC14	Cem1	SF1	CAE (SP1)	1.0
	RPC15	Cem1	SF1	PNS (SP2)	2.0
	RPC16	Cem1	SF1	PMS (SP3)	2.5
Optimal dosage +0.6%	RPC17	Cem1	SF1	CAE (SP1)	1.3
	RPC18	Cem1	SF1	PNS (SP2)	2.3
	RPC19	Cem1	SF1	PMS (SP3)	2.8

Table 6
Complete hydration enthalpy, clinker phases data [7] and cement values

Clinker phase or cement	$C_3A \geq$ ettringite	C_3S	C_4AF	C_2S	Cem1	Cem2	Cem3	Cem4
Complete hydration enthalpy (kJ/kg)	1672	517	418	262	490	555	434	381

The maximum of the thermal flux marks the beginning of the diffusion-controlled period.

3.4. Cross data

Ln(σ) as a function of the hydration coefficient (α). From the previous measurements, a log plot of the electrical conductivity as a function of the degree of hydration is presented in Fig. 2.

A linear trend, Eq. (3), is observed, until ln(σ) drops to a very low value. This drop expresses the discontinuity of capillary porosity. The associated degree of hydration, called percolation threshold (α_{perco}), is about 0.26, corresponding to about 4 days of hydration and to the consumption of half the initial water content.

$$\mathrm{Ln}(\sigma) = A_{\mathrm{v}} - B_{\mathrm{v}}\alpha \tag{3}$$

4. Influence of RPC mixtures on A_{v}, B_{v} and α_{perco}

For the 19 RPC studied, values of A_{v}, B_{v} and α_{perco} are given in Table 7.

4.1. Influence on A_{v}

A_{v} is the intercept of the linear trend, Eq. (3). A_{v} represents the logarithm of the electrical conductivity at the end of the dormant period ($\sigma_{\max}$). This value (A_{v}) mainly depends on σ_{sol}. In fact, before and during the dormant period, the term ($\phi\beta$) could be considered as constant. Therefore A_{v} strongly depends on RPC components according to [9]:

- initial SP dosage, (anionic molecule-based SP and associated cationic counterion), mainly for PNS (RPC 7, 12, 15, 18) and PMS (RPC 8, 13, 16, 19) which are more electrically charged than CAE (RPC 1, 11, 14, 17),
- cement composition, mainly soluble alkali (RPC 1, 4),
- quantity of soluble impurities and BET specific surface area of SF (RPC 1, 5).

4.2. Influence on B_{v}

B_{v} is the slope of the linear trend, Eq. (3). It represents the C–S–H efficiency to fill the capillary pores. Referring Eq. (1), B_{v} expresses how a same quantity of outer C–S–H is efficient to reduce the term ($\phi\beta$) by increasing the tortuosity and reducing the porosity, and how the associated bound water also reduces the term σ_{sol} by reducing the pore solution volume. This process is called self-desiccation. The shrinkage associated with this internal loss of water results in a mechanical decrease of the porosity, the term (ϕ) in Eq. (1). Thus B_{v} is also sensible to this action.

For the 19 RPCs studied, B_{v} averages 12.1 ln (Sm^{-1}), showing small variations (±2.7). The influence of the mineral matrix cannot be shown in this study (RPC 1, 4, 5), specially SF1 which has a higher pozzolanicity than SF2 gives a lower B_{v} value, 11.0 ln (Sm^{-1}) (RPC1) against 15.2 ln (Sm^{-1}) (RPC5). This remark shows that the pozzolanic reaction at 20C is far from being complete, as previously observed [10]. Therefore, at ambient temperature and young ages, the role of silica fume is mainly to increase the tortuosity of the capillary pores.

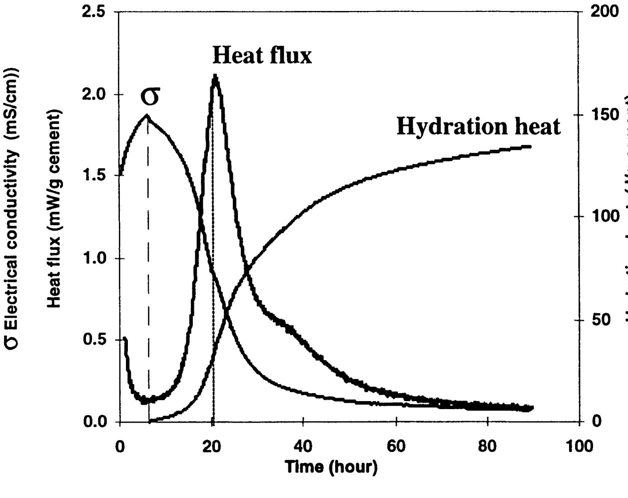

Fig. 1. Electrical conductivity (σ), heat flux and hydration heat as a function of time, RPC1, W/C=0.20.

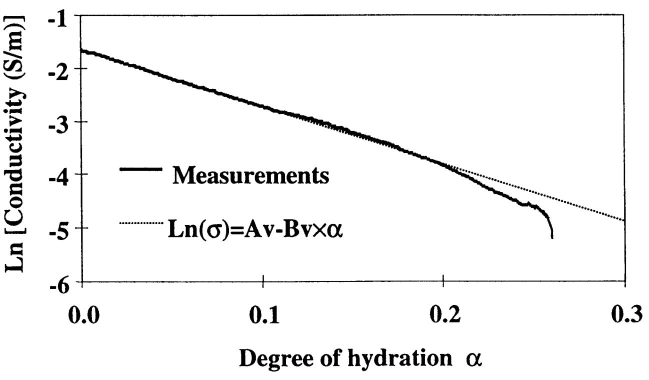

Fig. 2. Ln [electrical conductivity (σ)] as a function of the degree of hydration (α) RPC3, W/C=0.20.

Table 7
Composition of RPC studied

SP	RPC	A_v [ln (Sm^{-1})]	B_v [ln (Sm^{-1})]	α_{perco}
Optimal dosage	RPC1	−1.6	11.0	0.28
	RPC2	−1.8	11.0	–
	RPC3	−1.6	10.7	0.26
	RPC4	−1.3	12.0	–
	RPC5	−1.4	15.2	0.23
	RPC6	−1.7	10.1	0.27
	RPC7	−1.4	15.5	0.29
	RPC8	−1.3	13.1	0.30
	RPC9	−1.5	10.3	0.22
	RPC10	−1.0	10.2	0.23
Optimal dosage −0.3%	RPC11	−1.7	10.6	–
	RPC12	−1.4	12.6	0.24
	RPC13	−1.4	11.7	0.24
Optimal dosage +0.3%	RPC14	−1.7	12.6	0.23
	RPC15	−1.4	15.4	–
	RPC16	−1.3	12.9	–
Optimal dosage +0.6%	RPC17	−1.7	12.8	–
	RPC18	−1.4	11.2	–
	RPC19	−1.6	10.9	–
Average		−1.5	12.1	0.26
Standard deviation		0.19	1.7	0.026

Increasing the SP dosage, for example CAE (RPC 1, 11, 14, 17) and PNS (RPC 7, 12, 15, 18), does not significantly modify B_v.

In conclusion, and in first approximation, B_v can be considered as a characteristic of the granular packing.

4.3. Influence on α_{perco}

The percolation threshold (α_{perco}) represents the percent of hydrated cement necessary to make the capillary porosity discontinuous. For the 19 RPCs studied, only 11 α_{perco} have been measured. An average value of 0.26 was found, corresponding to 4 days of hydration. Accuracy on α_{perco} depends on isothermal regulation during approximately four days. Moreover at α=0.20, the curve no longer follows the linear trend very well. The pore solution volume becomes too low or the matrix is too tortuous to give a homogenous conductivity value. Therefore, our experimental set-up does not permit to conclude if and how α_{perco} depends on RPC formulation.

5. Influence of water/cement ratio on B_v and α_{perco}

5.1. Data

B_v and α_{perco} measured values for usual concrete (UC), high performance concrete (HPC) and reactive powder concrete (RPC) are given in Table 8. Water/cement ratios are respectively 0.60, 0.33 and 0.20. Values for UC and HPC were taken from previous work [11].

It can be observed that B_v increases with the decrease of the water/cement ratio, respectively 2.5, 5.5, 12.1 [ln (Sm^{-1})] for W/C=0.60, 0.33 and 0.20. The C–S–H efficiency to fill the capillary pores is higher for a low water content. However, B_v is arranged in the same order than the cement mass per unit volume, respectively 280, 450, 700 kg/m^3 for W/C=0.60, 0.33 and 0.20. To study the effect of an equal quantity of hydrated cement on the percolation process, normalization by the cement mass per unit volume is proposed. $B_{volumic}$ and $\alpha_{percovol}$ are the normalized values of B_v and α_{perco}.

$B_{volumic}$ follows the same range than B_v but the difference between each material is reduced, respectively 0.9,1.4,1.7 [ln (Sm) m^3] for UC, HPC and RPC.

Initial porosity (ϕ_i) values calculated from the water content (entrained air excluded) are almost equal for RPC and HPC, respectively 14.6% and 14.9% by volume. The observed difference on $B_{volumic}$, respectively 1.7 and 1.4 [ln (Sm) m^3] shows that self-desiccation and increase of tortuosity during hydration [term $\sigma_{sol}\beta$ from Eq. (1)] are more important in RPC than in HPC. If not $B_{volumic}$ should be identical for the two concretes because the initial porosity are identical [term ϕ from Eq. (1)]. As autogenous shrinkage increases with the decrease of the water content [12], this shrinkage could also explain the difference on $B_{volumic}$ between RPC and HPC.

The discontinuous capillary porosity is never reached for OPC (α_{perco}>1). For HPC and RPC, α_{perco} values are respectively 0.54 and 0.26, corresponding to a quantity of hydrated cement per cubic meter ($\alpha_{percovol}$) equal to 226 and 182 kg/m^3. These values are in agreement with the conclu-

Table 8

B_v, measured α_{perco} and associated quantity of hydrated cement

Material	W/C	Initial porosity ϕ_i (%)	Cement (kg/m^3)	B_v [ln (*Sm*)]	$B_{volumic}$ [ln (*Sm*).m^3]	α_{perco} (g/g)	$\alpha_{percovol}$ (kg/m^3)
UC	0.60	22.1	280	2.5	0.9	>1 [11]	>280
HPC	0.33	14.9	420	5.5	1.4	0.54 [11]	226
RPC	0.20	14.6	700	12.1	1.8	0.26	182

sions on $B_{volumic}$, self-desiccation and the increase of tortuosity are more important in RPC than in HPC.

5.2. Correlation between experimental and previsional values

Previsional values are issued from a three-dimensional digital-image-based simulation model of cement hydration developed by the National Institute of Standards Technology [13]. Simulations have been executed on pure C_3S pastes, without or with silica fume, up to SF/C_3S=30% by weight. Effects of sand particles and aluminates present in cement are not taken into account in the model. Experimental and simulated data about α_{perco} are given in Table 9 for W/C=0.20.

As previously shown, in RPC pozzolanic reaction does not seem to modify B_v and α_{perco}. This observation is consistent with the results given by Bentz and Garboczi [13]: the initial stages of the "pozzolanic" hydration (before 7 days) could have only minor effects on pore connectivity in comparison to later stages of hydration where percolation characteristics change rapidly. In RPC, capillary porosity becomes discontinuous at 4 days. In this case, simulation without silica fume seems to be closer to RPC behavior than with a complete pozzolanic reaction (0.26 against 0.19). Taking into account the accuracy, the measurement (α_{perco} around 0.26) fits fairly well with the prediction ($0.19 < \alpha_{perco} < 0.26$).

6. Perspective

Due to the linear trend, Eq. (3), a new method is proposed to continuously determine the hydration coefficient (α).

6.1. Equation

From the end of the dormant period (σ_{max}, α_{max}) to the point where the curve [ln(σ) as a function of α] diverges from the linear trend (σ_{div}, α_{div}), it is possible to obtain the degree of hydration by measuring the electrical conductivity. A combination of Eq. (3) between the end of the induction period and a given time (*t*) gives the following Eq. (4):

$$\alpha(t) = \frac{1}{B_v} \ln\left(\frac{\sigma_{max}}{\sigma(t)}\right) + \alpha_{max} \qquad (4)$$

Table 9

α_{perco} Measured values and modelled values for different SF contents

Measurement	Experiment	Simulation	
Paste	RPC	C_3S	C_3S+SF
Silica fume (%)	32.5	0	30
α_{perco}	0.26	0.26	0.19

6.2. Calibration

This calibration step is carried out at 20C. The quantity of hydrated cement before and during the dormant period (α_{max}) can be determined using a special calorimeter, where the water is injected into the sample using a syringe or with vacuum effect. In our study, α_{max} is neglected; in fact its value is very low (below 1%) [14]. For a given material, B_v is found using isothermal calorimetry and electrical conductivity (Fig. 2). Calibration also gives (σ_{div}, α_{div}) coordinates of the point, where the curve [ln(σ) as a function of α] no longer follows the linear trend (Fig. 2).

6.3. Measurement

Electrical conductivity measurements have to be extrapolated at 20C. The maximum of conductivity corresponds to σ_{max} (Fig. 1). Continuous recording of $\sigma(t)$ allows calculation of the degree of hydration, Eq. (4), as long as $\sigma(t) > \sigma_{div}$.

7. Conclusion

The granular packing of cementitious materials can be characterized during cement hydration using electrical conductivity and isothermal calorimetry. From both measurements, it is possible to find the percolation threshold (α_{perco}).

For RPC at W/C=0.20, the discontinuous capillary porosity is achieved when only 26% of cement has hydrated, instead of 54% for HPC (W/C=0.33).

This discontinuity is fairly well predicted by computer simulation models, assuming that the pozzolanic reaction is of minor importance on the pore connectivity at early ages.

A continuous determination of the degree of hydration using electrical conductivity is presented as a perspective in the study of RPC's.

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