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COMPOSITION OF REACTIVE POWDER CONCRETES

Pierre Richard, Marcel Cheyrezy
Scientific Division BOUYGUES, 78061 St Quentin en Yvelines, France

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ABSTRACT

Development of an ultra-high strength ductile concrete designated RPC (Reactive Powder Concrete), was made possible by the application of a certain number of basic principles relating to the composition, mixing and post-set heat curing of the concrete.
RPC 200, which can be used under job site conditions similar to those for conventional high performance concretes, can be used in the construction of prestressed structures incorporating no passive reinforcement.
RPC800 is suitable for precasting, and can achieve compressive strength values exceeding 600MPa. A value of 810MPa has been obtained with a mixture incorporating steel aggregate.

INTRODUCTION

Much research work has been done over the years, aimed at achieving high mechanical performance with cementitious matrix materials.

During the 1930s, Eugène Freyssinet demonstrated the advantage of applying pressure to fresh concrete during setting, in order to improve its strength (1). During the 1960s, strength values of 650MPa were obtained on compressed samples, heat-cured under elevated pressures (2).

More recently, two lines of research have been followed. The first concerns compact granular matrix concretes (DSP), with high superplasticizer and silica fume content, also incorporating ultra-hard aggregate (calcinated bauxite or granite) (3).

The other line of research relates to MDF (Macro Defect Free) polymer pastes (4). These pastes have very high tensile strength (150 MPa or more), in particular when mixed with aluminous cements (5).

An answer to the problem of the low ductility of the cementitious matrices obtained with these various techniques, was sought with the incorporation of steel fibres. Thus the SIFCON (Slurry Infiltrated Fibered Concrete) technique (6) involves filling the formwork with bulk fibres, and injecting a fluid mortar slurry.

A research programme was undertaken aimed at defining and developing ultra-high strength ductile concretes. These Reactive Powder Concretes (RPC) have compressive strengths ranging from 200 to 800MPa, and fracture energies up to 40 kJ m^{-2}.

RPC RESEARCH PROGRAM

Composition

The RPC research program was conducted with the application of the following basic principles:

- Enhancement of homogeneity by elimination of coarse aggregates;
- Enhancement of compacted density by optimization of the granular mixture, and application of pressure before and during setting;
- Enhancement of the microstructure by post-set heat-treating;
- Enhancement of ductility by incorporating small-sized steel fibers;
- Maintaining mixing and casting procedures as close as possible to existing practice.

Application of the first three principles produces a matrix with very high compressive strength, but with ductility no better than that of conventional mortar. The inclusion of fibres improves tensile strength, and also makes it possible to obtain the required level of ductility.

Measures relating to composition (homogeneity and granular compacted density) are the basis of the RPC concept, and are applied in all cases.

Measures relating to production (application of pressure and heat-curing) are optional measures designed to enhance performance. The advisability of applying these measures must be assessed for each RPC application, according to the technological difficulties involved (application of pressure) and/or their cost (heat-treatment).

This article presents a detailed analysis of the approach adopted for enhancement of the homogeneity and compacted density of RPC concretes.

Some typical compositions of RPC are given in Table 1.

TABLE 1
Typical RPC compositions (by weight)

	RPC 200				RPC 800	
	Non fibered		Fibered		Silica aggregates	Steel aggregates
Portland Cement	1	1	1	1	1	1
Silica fume	0.25	0.23	0.25	0.23	0.23	0.23
Sand 150 - 600 μm	1.1	1.1	1.1	1.1	0.5	-
Crushed quartz d_{50}=10μm	-	0.39	-	0.39	0.39	0.39
Superplasticizer (Polyacrylate)	0.016	0.019	0.016	0.019	0.019	0.019
Steel fiber L=12 mm	-	-	0.175	0.175	-	-
Steel fiber L=3 mm	-	-	-	-	0.63	0.63
Steel aggregates <800 μm	-	-	-	-	-	1.49
Water	0.15	0.17	0.17	0.19	0.19	0.19
Compacting pressure	-	-	-	-	50 MPa	50 MPa
Heat treatment temperature	20°C	90°C	20°C	90°C	250-400°C	250-400°C

Homogeneity enhancement

Conventional concrete is a heterogenous material, in which the aggregates (sand and gravel) form a skeleton of contiguous granular elements in the cementitious paste (cement, additives and water). The hardness of the aggregates is greater than that of the paste. For example, the Young's modulus for silica is 70GPa, compared with between 18 and 22MPa for the paste.

Heterogeneity-related problems are substantially reduced with RPC for the following reasons:

- Elimination of coarse aggregates, replaced by fine sand, (600 μm maximum);
- Improved mechanical properties of the paste;
- Reduction in the aggregate/matrix ratio.

Effect of aggregate size

Conventional concrete aggregates form a set of rigid inclusions. On application of a compression force shear and tensile stresses appearing at the paste/aggregate interface generate cracks in the paste. The size of these cracks is related to the extent of the zone under tensile or shear stress. In the case of a spherical inclusion, the size of the equatorial crack is directly proportional, to the diameter of the inclusion. For RPC, with a reduction in the size of the coarsest aggregate by a factor of about 50 (eg, 400 μm instead of 20mm), a major reduction is obtained in the size of microcracks of the following origins:

- Mechanical (external loads);
- Chemical (autogenous shrinkage);
- Thermo-mechanical (differential expansion between paste and aggregate under the effects of heat-treatment).

Effect of enhanced mechanical properties of the paste

RPC concretes invariably have Young's modulus values exceeding 50GPa, and which can go as high as 75GPa for those with the highest densities. In the latter case, we observe that the global modulus for the paste and aggregate is slightly higher than that for the silica aggregate. Thus the effect of mechanical heterogeneity has been totally removed, and even reversed.

In all cases, the increase in the Young's modulus for the RPC paste, by comparison with that of conventional cementitious pastes, tends to attenuate the effects associated with disturbance of the mechanical stress field.

Effect of limited sand content

The effects mentioned above are linked to aggregate size, and can be described as "meso-effects". Reduction of sand content represents a more global "macro-effect".

In a conventional concrete, the aggregates (sand and gravel) are the majority components in terms of volume, and form a rigid skeleton of contiguous granular elements. This means that a major proportion of paste shrinkage is blocked by the granular skeleton, with results in increased porosity.

In the case of an RPC, the volume of the paste is at least 20% greater than the voids index of non-compacted sand. Thus the aggregates used in RPC do not form a rigid skeleton, but a set of inclusions trapped in a continuous matrix. Paste shrinkage is blocked locally round each aggregate particle (with diminished consequences as a result of the size limitation effect mentioned above), whereas global shrinkage is not blocked by the rigid skeleton. Each grain can be transported by the paste, and can migrate with respect to its neighbors. This advantage only concerns structures where global shrinkage is unrestricted by any external source (eg, formwork).

PROCEDURES

Optimisation of the granular mixture

Optimisation of the granular mixture can be achieved by the use of packing models (7). For RPC mix design an experimental method has been prefered, based on the following principles:

- A mixture comprising a number of granular classes is obtained, with a tight granular range inside each class;
- Classes are separated, selecting a high ratio (exceeding 13) between mean diameter d_{50} for two consecutive granular classes;
- Cement/superplasticizer compatibility is studied, and optimum ratios are determined by rheological analysis;
- Only the least agglomerated fine powders are selected;

The main parameter for assessing the quality of the granular mixture is its water demand, i.e. the minimum quantity of water which must be added to the powders to obtain fluidification. The minimum water-to-binder ratio (W/B) obtained with the densest mixtures is 0.08. The term binder refers to cement and silica fume.

In reality, the voids index of the granular mixture corresponds to the sum of water demand and entrapped air. After selecting a granular mixture according to minimum water demand, optimum water content is analyzed using a more global parameter. This parameter is relative density d_0/d_S, where d_0 designates the density of the concrete at demoulding, and d_S designates the solid density of the granular mixture assumed to be compact (no water or air).

The variation in relative density with water content, expressed as the water-to-binder ratio, is shown in Fig. 1. Point A corresponds to the relative density obtained for minimum W/B ratio. Where the W/B ratio is increased slightly, the additional quantity of water replaces the entrapped air. The mass of the mixture then increases while its volume remains constant, and density d_0 and the relative density increases. When point B is reached, no entrapped air remains in the mixture. If the W/B ratio is then increased again, the additional water increases the volume of the mixture, and relative density d_0/d_S is reduced (point C).

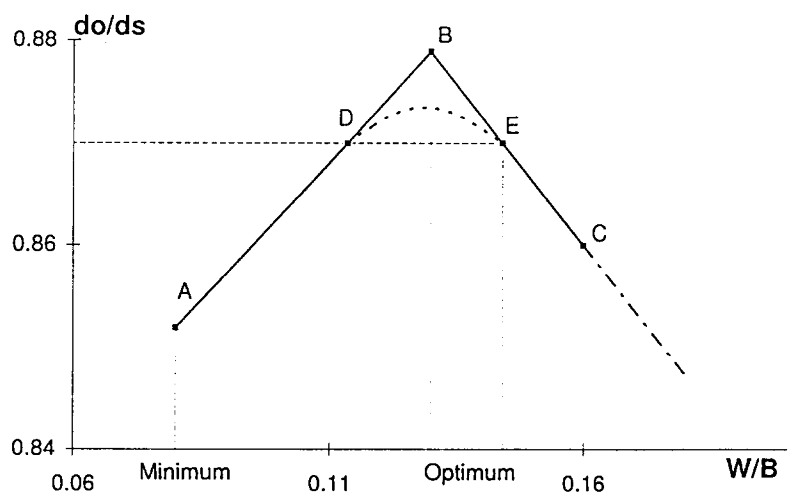

FIG. 1 : Variation in relative density with water content

There is therefore a maximum relative density level corresponding to a theoretical optimum water content. We observe that a given relative density can be obtained with two different water content values, situated on either side of the theoretical optimum (points D and E). The sample corresponding to point E provides better mechanical performance than the sample corresponding to point D, since the former contains less air and more water that will be partially integrated in the solid phase after hydration.

The theoretical optimum (point B) must therefore be shifted slightly towards the higher W/B ratio values, so that the effective mixture is situated on the BE segment of the graph, instead of AB.

Sample E has the additional advantage over sample D of possessing better rheological characteristics, ensuring easier flow of the concrete into the formwork.

The practical optimum water content value is therefore greater than the theoretical optimum, which is in turn greater than minimum water demand.

Slopes AB and BC are obtained very easily by computation. Curve ABC can therefore be determined from two experimental measurements only (for samples A and C). The analysis described only reflects the real situation partially, in particular for mixtures with maximum relative density (point B), the percentage of entrapped air being close to 2% rather than zero. Likewise, the experimental density curve is smoothed in the vicinity of the optimum state. However, this does not challenge the validity of the experimental approach for definition of optimum water content. The absolute and intrinsic nature of relative density makes this an essential parameter for comparison of different RPC formulations.

Relative density characterizes the quality of the granular mixture, water content and mixing and vibration efficiency in global terms. Measurement of d_0 is extremely simple, and is performed immediately after demoulding. This provides a parameter characterizing the quality of a test piece or structure at the production stage. Envelop figures for optimum compression strength values obtained for different relative density values of RPC concretes, with or without fibers, for both ambient and heat treated (90°C) specimens are given in Fig. 2. The compositions of the mixes giving the highest results are those indicated in Table 1.

Selection of granular components

The following granular components are used:
- Fine quartz sand aggregate;
- Cement;
- Crushed quartz;
- Silica fume.

Steel fiber constitutes a special inclusion.

<u>Sand</u>

Sand selection parameters to be defined are:
- Mineral composition;
- Mean particle size;
- Granular range;
- Particle shape;
- Mixture ratio by weight.

Insofar as mineral composition is concerned, quartz offers the following advantages:
- Very hard material;

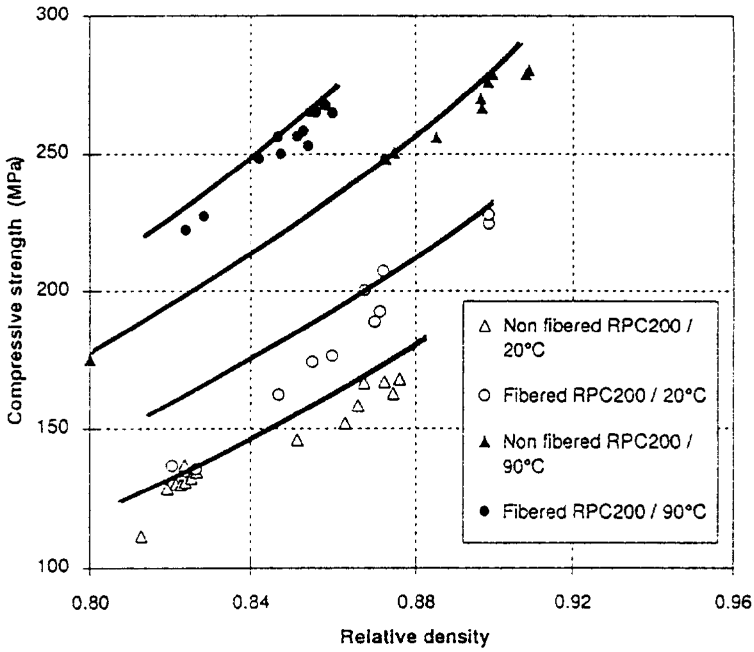

FIG. 2 : Envelop of optimum strength values obtained for different relative densities

- Excellent paste/aggregate interfaces;
- Readily available and low cost.

Mean particle size is defined in line with the homogeneity criterion, and the separation of granular classes criterion that have both already been described. The next lowest granular class is the cement, for which mean diameter d_{50} can vary between 11 and 15μm. A sand with a mean particle diameter of about 250μ m is therefore selected.

The particle size range is defined indirectly by the desirable maximum and minimum particle sizes. Maximum particle size is limited to 600μm, and for the minimum value, particle sizes below 150μm are avoided, in order to prevent interference with the largest cement particles (80-100μm).

Fine sand is obtained by screening crushed sand, where the grains are highly angular, or natural quarry sand, where the grains are more spherical. Both types of sand can be used for RPC. However water demand is slightly less for natural sand, which is therefore preferable.

Cement

The selection of cement cannot be dissociated from that of the superplasticizer. From the point of view of chemical composition, cements with low C_3A content give better results. As for particle size, we have observed that over-ground cements with a high Blaine fineness are not satisfactory, due to their high water demand. The best cement in terms of rheological characteristics and mechanical performance is a high-silica-modulus cement (8). However this type of cement has the disadvantage of a very slow setting rate, preventing its use for certain applications. Conventional quick-setting high performance cement offers very similar mechanical performance, despite a higher water demand.

The most efficient superplasticizers are polyacrylate-based dispersing agents, but which also exhibit a retarding characteristic which can present a problem for practical applications. The conventional superplasticizers selected for their compatibility with the cement give slightly poorer results. For the low w/c ratios used for RPC concretes, the optimum superplasticizer ratio is high (solid content of approx. 1.6% of cement content).

Silica fume

The silica fume used in RPC concretes has three main functions:

- Filling the voids between the next larger class particles (cement);
- Enhancement of rheological characteristics by the lubrication effect resulting from the perfect sphericity of the basic particles;
- Production of secondary hydrates by pozzolanic reaction with the lime resulting from primary hydration.

The following parameters are used for silica fume characterization:

- Degree of particle aggregation;
- Nature and quantity of impurities;
- Basic particle size.

The main quality of a silica fume is the absence of aggregates. This leads to the use of non-compacted silica fumes. Slurry cannot be used, as the quantity of water contained in the slurry exceeds the total quantity of water required for the mixture. The most injurious impurities are carbon and alkalis (9).

Particle size is a secondary factor. Indeed the best results are obtained with silica fume procured from the zirconia industry, being free from impurities and totally disaggregated. However Blaine fineness is lower than that for conventional fumes ($14m^2/g$ compared with $18m^2/g$). On the other hand, an impurity-free fume with a high Blaine fineness value ($22m^2/g$) produced mediocre results, due to the aggregation of the finest particles.

Typically the fume/cement ratio used for RPC is 0.25. This ratio corresponds to optimum filling performance (10) and it is close to the dosage required for complete consumption of the lime resulting from total hydration of the cement. However, cement hydration is incomplete in an RPC concrete, and the available quantity of silica fume is more than required by the pozzolanic reaction.

Crushed quartz

Crushed crystalline quartz powder is an essential ingredient for heat-treated RPC concretes. Maximum reactivity during heat-treating is obtained for a mean particle size of between 5 and 25μm (11). The mean particle size of the crushed quartz used for an RPC is 10μm, and is therefore in the same granular class as the cement.

The ratio by weight adopted corresponds to the stoechiometric optimum for conversion of amorphous hydrates into tobermorite characterized by a C/S molar ratio of 5/6 = 0.83. This is achieved with a silica/cement ratio of 0.62. This ratio is obtained by adding silica fume and crushed quartz as a complement (see Table 1).

Application of pressure

We have seen that compressive strength increases with density. An effective way of increasing density is to apply a confining pressure force to the fresh concrete. This application of pressure has three favorable effects, according to the method and length of application:

Reduction of entrapped air

The application of pressure eliminates or considerably reduces air bubbles in a few seconds.

Excess water removal

If pressure is applied for several minutes to fresh concrete for which the formwork is not totally watertight, water is expelled via the formwork interstices. These must be sufficiently narrow to prevent extrusion of the finest solid particles. This can be achieved simply by removing the waterproof seals of metal moulds. The efficiency of the device is checked simply by visual inspection of the exudate, which should remain clear.

Application of a pressure of 50MPa to a test piece with a diameter of 7cm for 30 minutes, can eliminate between 20 and 25% of the water initially introduced during mixing. Given the low w/c ratio values for RPC, this result is highly significant, and corresponds to an increase of more than 2% in relative compacted density.

The extracted water must flow from within the sample, and therefore the water extraction efficiency depends on sample size, and the position of the extraction points.

Chemical shrinkage compensation

If the applied pressure is maintained throughout the setting phase for the concrete, typically for between 6 and 12 hours after mixing, part of the porosity appearing in the sample as a result of chemical shrinkage can be eliminated.

The pressure applied during setting induces microcracking in the sample, identified by measuring the dynamic elasticity modulus on demoulding. This microcracking is due to the fracture of rigid bridges created during setting, and expansion of the aggregate when the pressure is released. The microcracks subsequently heal as the test piece hardens.

Taken together, the effects described above lead to relative density gains exceeding 6%.

Compressive strength is highly dependent on the relative compacted density at demoulding. Results for pressurized samples of identical composition which have undergone identical heat-treating at 400°C are indicated on Fig. 3. Conversely, tensile strength is only marginally enhanced by the application of pressure.

Microstructure enhancement by heat-curing

The procedure adopted for enhancing the microstructure and mechanical performance of RPC is described in detail in Ref. (12). Heat-treating is performed after the concrete has set, by simply heating at ambient pressure.

Heat-treating at 90°C substantially accelerates the pozzolanic reaction, while modifying the microstructure of the hydrates which have formed. However these hydrates remain amorphous.

High temperature heat-treating (at between 250 and 400°C), only applicable to fibered RPC, leads to the formation of crystalline hydrates (xonotlite), accompanied by major dehydration of the hardened paste (13).

Ductility enhancement by the incorporation of fibers

The behaviour of RPC matrices is purely linear and elastic, corresponding to a fracture energy not exceeding 30J m^{-2}. Fibers must be added to enhance RPC ductility. The straight

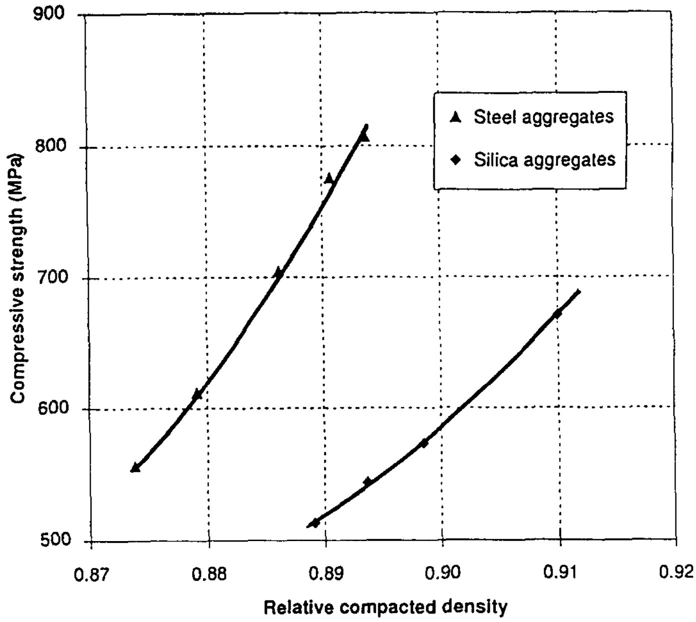

FIG. 3 : Variation in strength with relative density of RPC 800 concretes

steel fibers used are 13mm long, with a diameter of 0.15mm. The fibers are introduced into the mix at a ratio of between 1.5 and 3% by volume. The economic optimum corresponds to a ratio of 2%, or about 155kg/m^3.

For RPC concretes heat-treated at 250°C and above, enhanced mechanical performance (compressive and tensile strength) is obtained with a shorter fiber (less than 3mm) of irregular form. In this case, the fracture energies obtained are sharply reduced, while compressive strength is increased. A compressive strength of 810MPa has been achieved on a 6cm diameter cylinder, for an RPC incorporating steel aggregates (see composition in Table 1).

Intermediate results are obtained by mixing the two types of fibers.

RESULTS

Mechanical performance

RPC concretes constitute a new family of materials, for which the respective applicational fields depend on performance, cost and ease of mixing and placement. This family includes two types of RPC, designated RPC 200 and RPC 800, which offer interesting applicational possibilities in different areas. Mechanical properties for the two types are summarized below:

<u>RPC 200</u>

- Pre-setting pressurization	None
- Heat-treating	20 to 90°C
- Compressive strength	170 to 230MPa
- Flexural strength	30 to 60MPa

- Fracture energy	20,000 to 40,000J. m^{-2}
- Ultimate elongation	5,000 x 10^{-6} to 7,000 x 10^{-6}m.m^{-1}
- Young's modulus	50 to 60GPa

The mean compressive stress obtained for a series of 75 samples of identical composition and heat-treated at 90°C was 218 Mpa with a standard deviation of 7.5 MPa.

RPC 800

- Pre-setting pressurization	50MPa
- Heat-treating	250 to 400°C
- Compressive strength:	
using quartz sand	490 to 680MPa
using steel aggregate	650 to 810MPa
- Flexural strength	45 to 141MPa
- Fracture energy	1,200 to 20,000J. m^{-2}
- Young's modulus	65 to 75GPa

Production and application conditions (mixing and vibration) for RPC 200, for which the pressurization technique is not used, are close to those of a conventional high performance concrete. By reason of its high ductility, utilisation of this material is envisioned for structures not incorporating traditional passive reinforcement. For elements submitted to bending (beams and slabs) or tension (truss elements), dissymmetry in RPC's behavior in tensile and compressive strength can be compensated by the utilization of prestressing techniques. In structures of this type, the main tensile forces are taken up by the prestressing, whereas secondary tensile stresses and all compressive loads are taken up directly by the concrete itself (14). Structures configured in this way can be about three times lighter than equivalent structures fabricated with conventional concrete.

The combined effects of the elimination of reinforcement, reduction of permanent loads by lightening the structure, and reduction of the quantities of concrete used, generate major cost savings.

The replacement of conventional concrete with RPC also produces a substantial reduction in the consumption of mineral resources (sand and gravel), the massive extraction of which is causing a growing environmental concern.

RPC 800 requires the application of pre-setting pressure and heat-treating at 250°C, and can only be used for production of precast elements. We can thus foresee the utilisation of RPC 800 in place of steel, in the manufacture of mechanical parts. This material also has excellent projectile impact resistance properties, and can be employed for hardening military structures or equipment.

Apart from their exceptional mechanical properties, RPC concretes have an ultra-dense microstructure, giving advantageous waterproofing and durability characteristics. These materials can therefore be used for industrial and nuclear waste storage facilities.

CONCLUSIONS

Elimination of coarse aggregates combined to optimization of the granular mixture allows the obtention of an homogenous and dense cementitious matrix that exhibits high mechanical performances.

- Application of a confining pressure to the fresh concrete combined to excess water removal further improves the density. Induced microcracking does not impede compressive strength enhancement.

- Addition of small size (⌀ = 0.15 mm L = 13 mm) steel fibers at a ratio of 2-2.5% per volume gives to RPC a ductile behavior.

REFERENCES

1. E.Freyssinet, Cem. Concr. Manufacture., Vol. 9, p. 71, 1936
2. D.M. Roy, G.R. Gouda, Cem.Concr. Res., Vol. 3 (6), p. 807-820, 1983
3. H.H. Bache, Densified cement ultrafine particle-based materials. 2nd International Conference on Superplasticizers in Concrete, Ottawa, p. 33, June 10-12, 1981
4. N.M. Alford, G.W. Groves , D.D. Double, Cem. Concr. Res., Vol. 12 (2) p.349-358 1982
5. J.D. Birchall, Phil. Trans. R. Soc. Lond. A310, p. 31-42, 1983
6. D.R. Lankard, D.H. Lease, Am. Ceram. Soc. Bull., Vol. 61 p. 728, 1982
7. F. De Larrard, Th. Sedran,Optimization of ultra-high-performance concrete by the use of a packing model, Cem. Concr. Res., Vol. 24, (6) p. 997-1008, 1994
8. P.C. Aitcïn, S.L. Sarkar, R. Ranc, C. Levy, A high-silica-modulus cement for high performance concrete, Advanced Cementitious Materials. Am. Ceram. Soc., p. 103-21, 1991
9. F. De Larrard, Ultrafine particles for the making of very high strength concretes, Cem. Concr. Res., Vol. 19, (1) p. 161-172, 1989
10. S. Seki, M. Morimoto, N. Yamane, Recherche expérimentale sur l'amélioration du béton par l'incorporation de sous-produits industriels, Annales de l'ITBTP N°.436, p. 16-26, July-August 1985
11. C.A. Menzel, Journal of ACI Proceedings Vol. 31, p. 221-244, 1934
12. P.Richard, M. Cheyrezy, Les bétons de Poudres Réactives, Annales de l'ITBTP, Paris, Vol 532, p. 8-35, Avril-Mai 1995
13. M. Cheyrezy, V. Maret, L. Frouin, Microstructural analysis of Reactive Powder Concrete, Cem. Concr. Res. (Accepted)
14. P. Richard, M. Cheyrezy, Pretensioned beam without conventional reinforcement FIP notes, 1995/1 (in press).