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# MICROSTRUCTURAL ANALYSIS OF RPC (REACTIVE POWDER CONCRETE)

Marcel Cheyrezy*, Vincent Maret*, Laurent Frouin**
*Direction Scientifique BOUYGUES, 78061 St Quentin en Yvelines, France
**Rhône-Poulenc-Recherche, 98308 Aubervilliers, France

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## ABSTRACT

Reactive Powder Concretes (RPC) are characterized by high silica fume content and very low water to cement ratio. Granulometry and heat treatment were optimized to obtain excellent mechanical and durability properties. The study of several RPC compositions by Mercury Porosimetry, Thermogravimetric Analysis and X-ray diffraction made it possible to better understand their microstructural properties depending on their heat treatment. Influence of temperature on hydration and pozzolanic reaction were examined. For high temperature, the presence of a crystal hydrate, xonotlite, was observed. Mercury Porosimetry also showed that a minimum porosity could be obtained with selected heat treatment.

## INTRODUCTION

Reactive Powder Concretes (RPCs) exhibit very high mechanical and durability properties (1, 2). Their composition is OPC cement, silica fume, aggregates with very fine granulometry, sand with average grain diameter of 250µm, crushed quartz (average grain diameter of 10µm). In order to increase concrete ductibility and flexural strength, metalic fibers can be added.

The basic formulation is OPC: 1; Silica Fume: 0.25; Sand: 1.1; W/B (water to binder ratio): 0.12. Some formulations contain crushed quartz (or 40% by weight of cement) or steel fibers (approximately 2% in volume).

OPC composition is approximately: $C_3S$: 60%; $C_2S$: 22%; $C_3A$: 3.8%; $C_4AF$: 7.4%.

RPC properties are improved by two means. Fresh RPC samples may be pressed. Heat treatment is applied to samples once demoulded. In the case of pressed samples, pressure is applied before and during the setting period. In this paper, this parameter will be referred to as setting pressure. The two parameters, heat treatment temperature and setting pressure were studied on the following samples:

## MATERIALS

B20°C/SC, Basic formulation heated at 20°C, soft cast (setting pressure, 1atm)
B20°C/P, Basic formulation heated at 20°C, pressed (setting pressure, 310atm)
B90°C/SC, Basic formulation heated at 90°C, soft cast
B90°C/P, Basic formulation heated at 90°C, pressed (setting pressure 625atm)
BQ200°C/SC, Basic formulation with crushed quartz heated at 200°C, pressed (setting pressure 625atm)
BF 250°C/SC, Basic formulation with steel fibers heated at 250°C, soft cast
BQF400°C/SC, Basic formulation with crushed quartz and steel fibers heated at 400°C, soft cast
BQF 400°C/P, Basic formulation with crushed quartz and steel fibers heated at 400°C, pressed (setting pressure 625atm)

RPC microstructural properties as a function of heat treatment temperature and pressure applied to the concrete before and during setting were studied by thermogravimetric analysis and XRD. Hydration and pozzolanic reaction were also better understood. High temperature-cured RPCs were shown to contain xonotlite. RPC porosity was analyzed.

## ANALYSIS

### Thermogravimetry, x-ray-diffraction

Samples were measured on a NETZSCH ATS 429 thermogravimetric analyzer, under dry air atmosphere. A temperature range between 20°C and 1200°C with a 10°C per minute heating rate was selected. Results were independent of measurement atmosphere (air or argon). XRD spectra were performed by a PHILIPS PW 1710 diffractomer (radiation Cu $K\alpha$). Samples were 5mm high by 10mm diameter cylinders crushed by a hammer. The grain size was approximately 20μm.

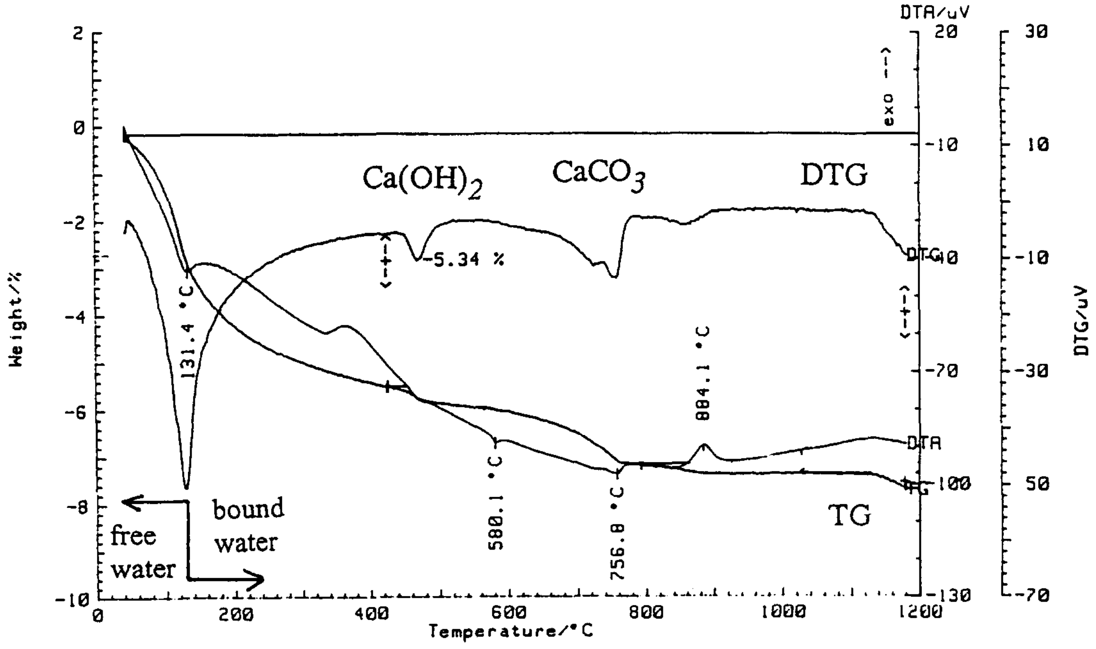

FIG 1 : Thermogravimetric curve of B20°C/SC

RPCs with varied treatment conditions (temperatures between 20°C and 400°C and setting pressure between 1atm and 620atm) were analyzed by thermogravimetry.

The thermogravimetric curve of sample B20°C/SC is given in Figure 1.

Interpretation of thermogravimetric results remains widely debated (3) especially concerning water in concrete. We have considered in this paper that the weight loss between 20°C and the temperature of the first DTG (Derivative thermogravimetric curve) peak was due to loss of water not chemically bound in hydrates. In the present paper we will refer to it as free water. For temperatures higher than that of the first DTG peak, water losses are due to structural water (dehydration of CSH, dehydroxylation of portlandite). These definitions however conventional, are valid for the comparative study of RPC samples analyzed in this text. The DTG peak between 420°C and 500°C was identified as dehydroxylation of portlandite $Ca(OH)_2$. The DTG peak between 750°C and 850°C was attributed to decarbonation of calcite $CaCO_3$ (4, 5).

For each sample, total water content was evaluated as the total weight loss between 20°C and 1200°C minus the weight losses due to portlandite dehydroxylation and calcite decarbonation. Free water (weight loss between 20°C and the first DTG peak) and bound water (constitutive of CSH hydrates) add up to total water content.

The total lime content can be computed by integration of DTG peaks relative to the dehydration of $Ca(OH)_2$ (420°C - 500°C) and the decarbonation of calcite (750°C - 800°C). Since the cement composition is known, it is also possible to compute the bound water quantity as well as the portlandite quantity that would be produced by complete hydration ($MP_C$). It was considered starting from strandard hydration equations of OPC that complete hydration of 1g of $C_3S$ yields 0.36g of portlandite and hydration of 1g of $C_2S$ yields 0.12g of $C_2S$. Here for 100g of the OPC used ($C_2S$: 60%; $C_2S$.: 22%) primary hydration of $C_3S$ and $C_2S$ gives $MP_C = 100 \times 0.60 \times 0.36 + 100 \times 0.22 \times 0.12 = 24.2$g. The effective amount of portlandite ($MP_O$) is then computed by multiplication of $MP_C$ by the hydration rate. The latter may be estimated as the ratio of the bound water quantity, as measured by thermogravimetry, to the bound water quantity produced by complete hydration of cement. For RPC samples analyzed in this paper, hydration rates vary from 40% to 60%. The pozzolanic ratio, pzr, was defined as follows

$pzr = 1 - MP/MP_0$
pzr, pozzolanic ratio
MP, Portlandite mass contained in sample
$MP_0$, Portlandite mass produced by hydration of cement

The progression of the pozzolanic reaction (reaction between silica fume and $Ca(OH)_2$ to form CSH hydrates) can be investigated through pzr. Pzr values close to 1 indicate high pozzolanic activity. If pzr=1, all portlandite produced by hydration was consumed by pozzolanic reaction.

High temperatures lead to a higher bound-water percentage. At 400°C, no more free water remains in concrete (Fig. 2). This is highly favorable to durability properties since aggressive agents can be carried into concrete by free water. It can also be concluded from figure 2 that setting pressure has little influence on the distribution of total water content between free water and bound-water. It should be noted however that part of the mixing water is expelled by pressure applied during setting. Total water content of pressed concretes is therefore smaller than that of soft cast concretes.

The evolution of the pozzolanic ratio, pzr, versus curing conditions is shown in Figure 3. Pzr is seen to increase with curing temperature with little influence exerted by setting pressure. This confirms that pozzolanic activity is increased by increasing curing temperatures.

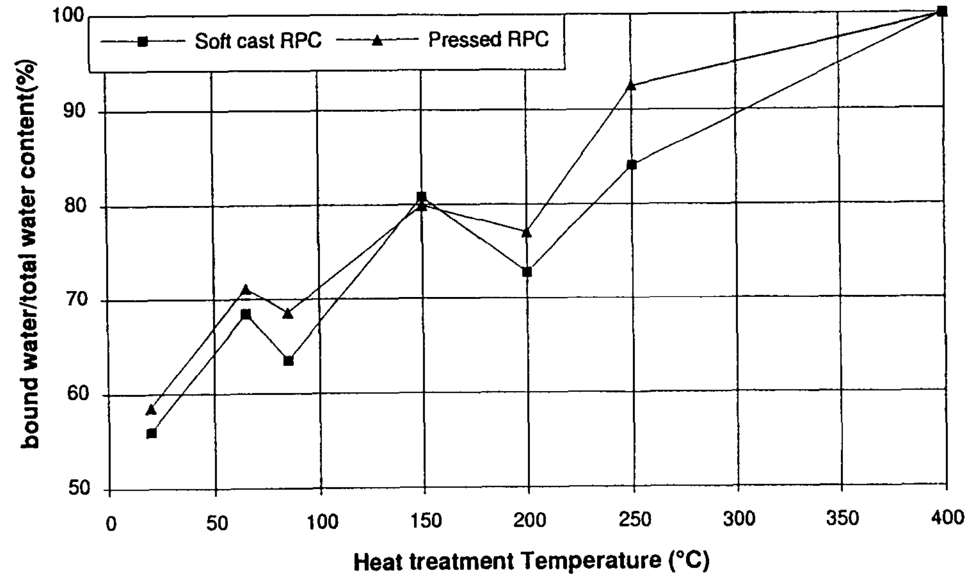

FIG 2 : Bound-water percentage in RPC versus heat treatment temperature

For temperatures higher than, or equal to 250°C almost all portlandite formed by hydration of cement is consumed by pozzolanic reaction. Pzr curves are similar for pressed samples and soft cast ones. It can be noted at 150°C that the sample contains $C_2SH\alpha$ whose thermogravimetric water-loss peak is located in the same temperature range as that of $Ca(OH)_2$. This causes an important increase of this peak. This phenomenon only occured for samples with heat treatment of 150°C which corresponds to the stability of $C_2SH\alpha$. Furthermore, mechanical properties of these samples were deteriorated. In this case, the pzr value was impossible to estimate.

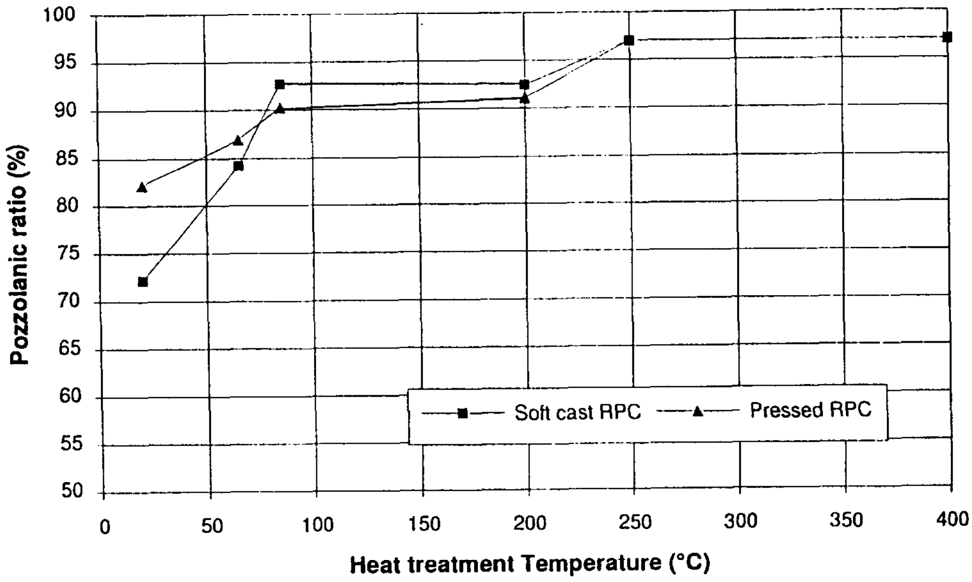

FIG 3 : Pozzolanic ratio versus heat treatment temperature

Thermogravimetric analysis shows that in RPC a high proportion of cement remains unhydrated (the degree of cement hydration varies from 40% to 60%). This is confirmed by XRD spectra of samples B20°C/SC; BQ200°C/SC, BF250°C/SC and BQF400°C/P displayed in Figure 4. In those spectra, $C_3S$ and $C_2S$ peaks characteristic of unhydrated cement, are detected, even for high curing temperatures.

Furthermore a $Ca(OH)_2$ peak (d = 4.9 Å, intensity 74%) is present for a heat treatment

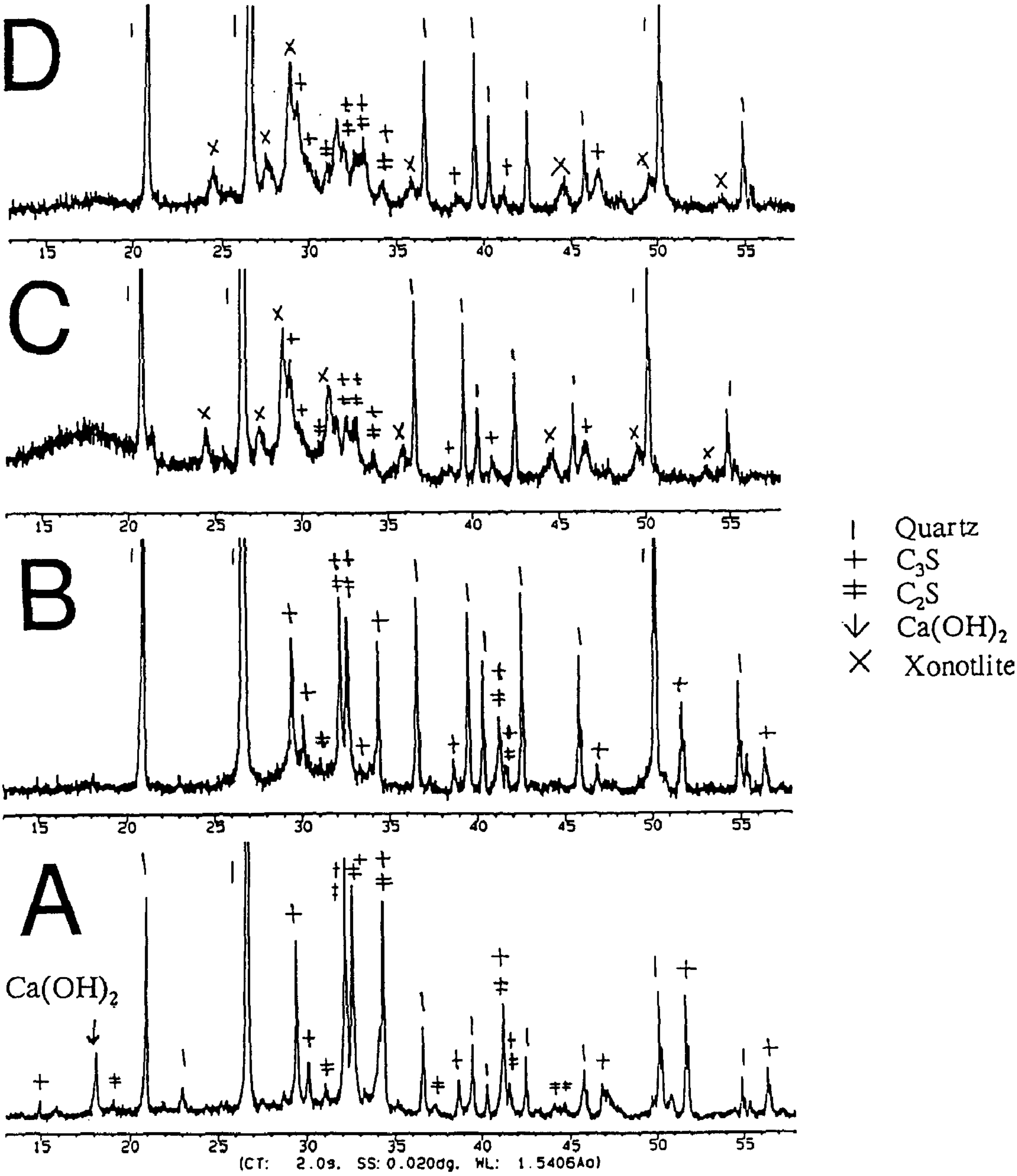

FIG 4 : XRD spectra of RPC samples
4A : B20°C/SC; 4B : BQ200°C/SC;4C : BF250°C/SC; 4D : BQF400°C/P

temperature of 20°C but cannot be identified for temperatures of 200°C or higher (see Figure 4). This confirms the activation of pozzolanic reaction with temperature.

It should also be noted that ettringite was not observed by XRD. None of its characteristic peaks were identified in Figure 4. This phenomenon could be explained by the small $C_3A$ content (3.8%) of the cement used, as well as by the very low water to cement ratio.

Thermogravimetric curves of BQ 400°C/P samples are shown in Figure 5. The DTG peak at 800°C was attributed to the water loss of a crystalline hydrate, xonotlite. Previous research has established that thermograms of xonotlite exhibit a DTG peak in the same range of temperatures (6).

Furthermore, xonotlite is only detected on sample taken from the inner part of test specimen of BQ 400°C/P (Fig. 5). It is absent from a sample taken from the periphery of the same specimen (Fig. 5). This leads to the conclusion that hydrothermal conditions necessary for the formation of xonotlite were spontaneously fulfilled in the inner part of the test piece. It can be supposed that water extracted from hydrates is trapped in the center of the test specimen during transient heating, due to extremely low RPC porosity (see Mercury porosimetry paragraph).

The presence of xonotlite was confirmed by XRD as can be seen in Figure 4 where xonotlite is present in samples cured at 250°C and 400°C. For temperatures of 200°C or less, xonotlite is not detected.

Water extracted from the basic RPC formulation as a function of the temperature steps to which test sample was subjected is displayed in Figure 6. The duration of each temperature step (a few hours) is such that the sample remains in transient regime during the entire process. A large quantity of water is extracted between 230°C and 250°C (Fig. 6). This phenomenon can be attributed to the transformation of hydrates with C/H (CaO to $H_2O$) ratio close to unity (and even C/H = 1 for tobermorite $C_5S_6H_5$) into xonotlite ($C_6S_6H$, C/H = 6). The temperature of the transformation is consistent with XRD results (Fig. 4).

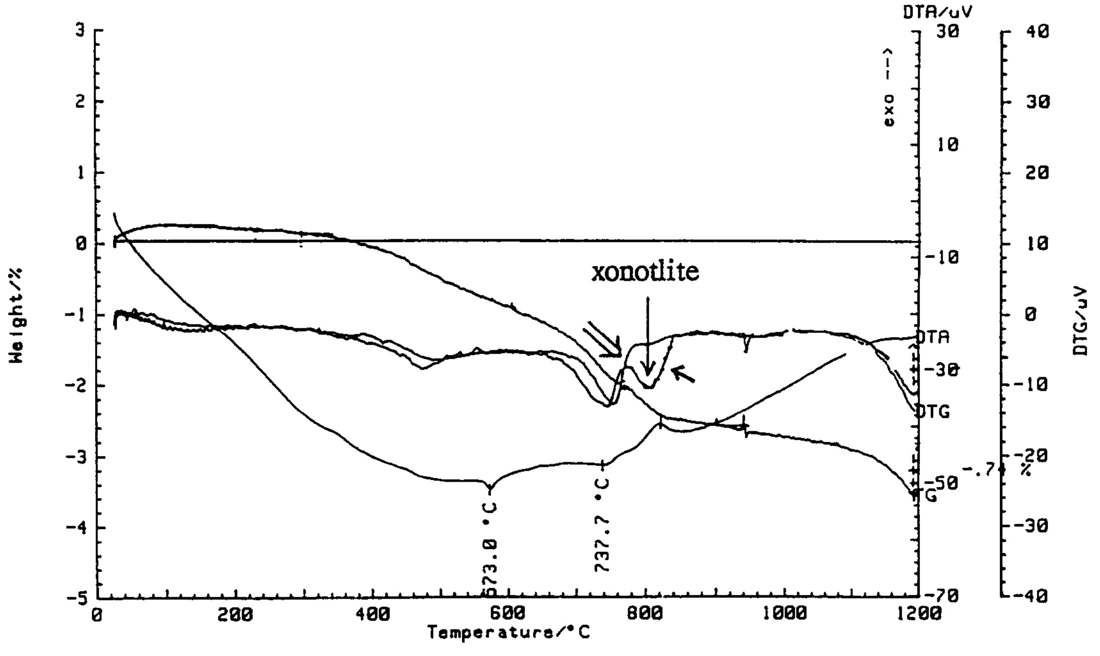

FIG 5 : Thermogravimetric curve of BQ400°C/P
→ DTG of sample taken from the inner part of test piece
⇒ DTG of sample taken in periphery of test piece

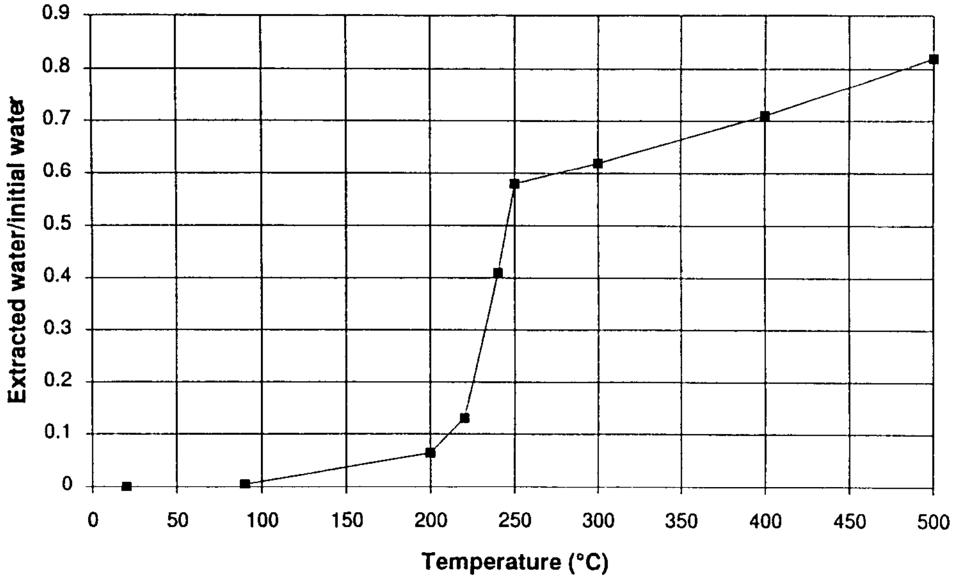

FIG 6 : Water extracted from RPC versus heat treatment temperature

It can be concluded from this study that RPC is a partly unhydrated concrete in which increased heat treatment temperatures enhance the proportion of bound water and the pozzolanic activity. For temperatures of 250°C and above a crystal hydrate, xonotlite is formed.

### Mercury porosimetry

Porosimetric measurements were carried out on a MICROMERITICS AUTOPORE 9220 porosimeter. 3.75nm to 300μm pore sizes are investigated by this technique. Samples are splinters

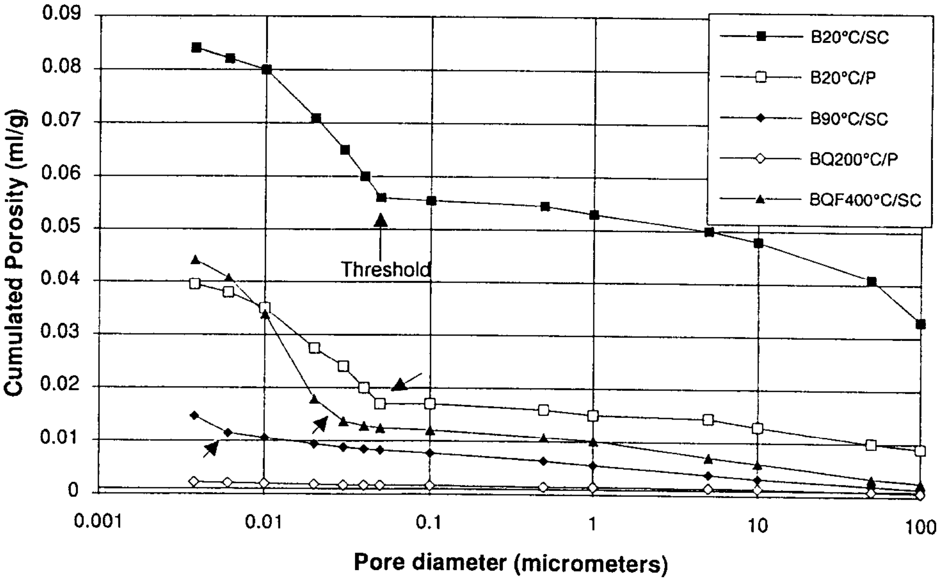

FIG 7 : RPC cumulative porosity versus pore diameter taken from cylindrical test-specimens (diameter 70mm, height 140mm) which are oven-dried at 120°C for 15 hours.

The mercury intrusion curves of samples B20°C/SC; B20°C/P; B90°C/SC; BQ200°C/CP; BQF400°C/SC are displayed in Figure 7. Figure 8 shows 3.75nm - 100μm cumulative porosity (cumulative porosity for pore diameter from 3.75nm to 100μm) of RPC versus curing conditions. 3.75nm to 100μm cumulative porosity is given as a percentage of sample volume. For all samples tested in this study, the cumulative porosity never exceeds 9%.

RPC porosity consists mainly of pores with diameter smaller than a threshold value (Fig. 7). A reduction of cumulative porosity corresponds with a decrease in the threshold value (see B20°C/SC, B90°C/SC in Figure 7). For some samples (BQ200°C/SC, Fig. 7), the threshold value is so small that it cannot be detected by mercury intrusion. In that case, the cumulative porosity is also negligible. The slight slope that can be observed for BQ200°C/SC sample (Fig. 7) is due to the compressibility of mercury. Figure 9 displays the porosity threshold of RPC versus heat treatment temperature.

From 20°C to 65°C, setting pressure does not affect the 3.75nm - 100μm cumulative porosity. This does not mean that porosimetric curves are totally similar. For instance, 100μm cumulative porosity of B20°C/SC sample is higher than that of B20°C/P (Fig. 7). The role of setting pressure is then to eliminate the air trapped in sample and to compact the sample. A portion of free water is also eliminated. In that range of temperature, the porosity threshold is not modified.

For temperatures between 80°C and 200°C, lower porosity is obtained for pressed samples (Fig. 8). In this range of temperatures, the cumulative porosity and threshold pore size both decrease (see B90°C/SC, BQ200°C/P on Figure 7 and Figure 9). It was shown previously that an increase in heat treatment temperature led to higher bound water percentage and intensification of pozzolanic activity. Hydrates produced by the latter do not decrease overall porosity, due to chemical shrinkage. Nevertheless, they lead to a decrease in intermediate (3.75 nm - 100μm)

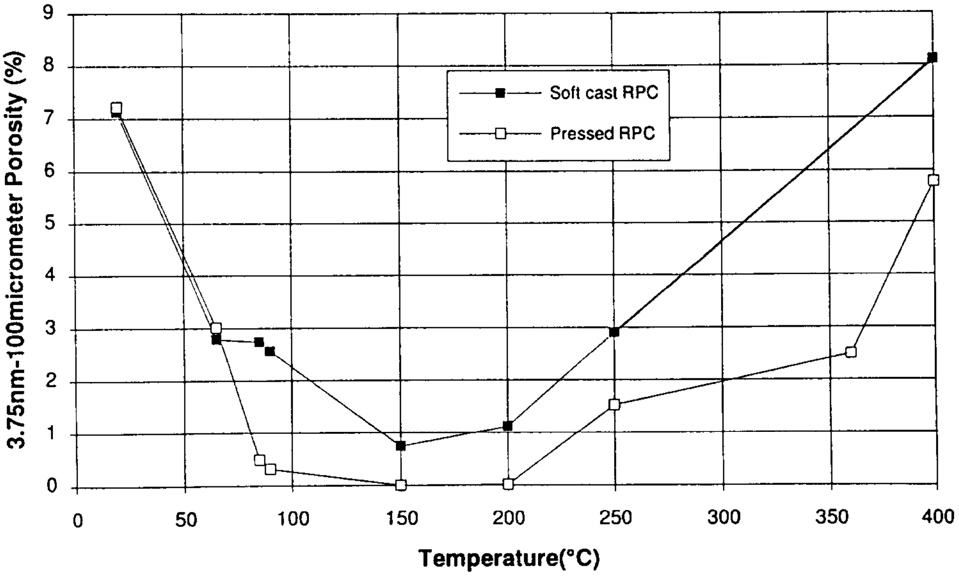

FIG 8 : 3.75nm - 100μm cumulative porosity versus heat treatment temperature

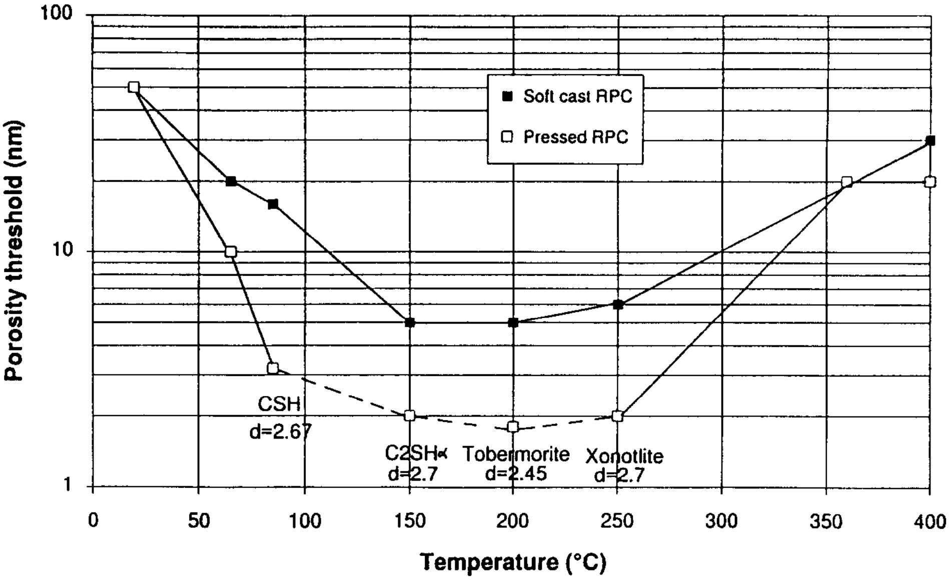

FIG 9 : Porosity threshold of RPC versus heat treatment temperature

porosity. The greater part (B 90°C/SC, Fig. 7) if not the whole porosity (BQ 200°C/P, Fig. 7) corresponds in that case to pore diameters smaller than 3.75nm.

For heat treatments at 200°C, samples were shown to exhibit a residual expansion after return to a temperature of 20°C. This expansion was not due to cracking, but rather can be attributed to the formation of a hydrate exhibiting relatively low density, tobermorite (d = 2.45). However, no clear evidence of crystalline 11 Å tobermorite was shown by XRD. It is thus more likely to be in presence of CSH which tobermoritic characteristics. For RPC, we can estimate (7) that CSH hydrates have a density of 2.67. It can be supposed that the production of a low density hydrate leads to a better filling of vacant space. A minimum value of porosity threshold is then obtained (Figu. 9). So as to ascertain this hypothesis, a more sensitive technique than Mercury Intrusion is to be used.

For temperatures of 250°C and above, porosity is increased, as well as the threshold pore size (see BQ200°C/P and BQF400°C/SC in Figure 7). A change in the nature of porosity was noted. This change can be attributed to the formation of xonotlite which is accompanied by formation of water. Xonotlite contains fewer water molecules (C/H = 6) than CSH hydrates (C/H = 1 approximately). The evacuation of this water due to high temperature can explain the change observed in the nature of porosity. Between 250°C and 400°C, additional extraction is observed (Fig. 6) but it is less intense. Still, the effect on intermediate porosity and porosity threshold is high.

It can be concluded that heat treatment conditions greatly affect porosity. A minimum value of porosity, corresponding to very small pore diameters, is obtained for pressed RPC with heat treatments between 150°C and 200°C.

## CONCLUSION

RPC microstructure depends on heat treatment conditions and pressure applied before and during setting. Thermogravimetric and XRD studies made it possible to gain better understanding of the microstructural changes induced by these procedures. It was shown that an increase in temperature led to a change in the microstructure of CSH hydrates. Pozzolanic activity is also intensified by temperature. Between 200°C and 250°C, the formation of a crystal hydrate, xonotlite, was observed.

Porosimetric studies by mercury intrusion demonstrated the very low porosity of RPC, which never exceeds 9 % in volume in the pore diameter range of 3.75nm to 100μm. It is nil in that range for pressed RPC cured between 150°C and 200°C.

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