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Macrodefects and Microdefects within Porous Cement Pastes

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Macrodefects and Microdefects within Porous Cement Pastes

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Abstract. It is shown that the mechanical strength of cement matrix (hydrated cement paste) is a result of competitive interplay between macrodefects and microdefects. The dominance of one of these two kinds of defects depends not only on their sizes but also on their numbers. The cross-over between dominances of macrodefects or microdefects is determined both by a critical number of defects and by their critical size, which depends on the mechanical parameters of the materials.

1. Introduction

Cementitious materials have been used since Roman times. Despite their great improvement in the last two centuries, they still hide various puzzles that await thorough solutions. One of these puzzles is the *distinct difference* between compressive and tensile/flexural strengths, which prevents ordinary concretes from serving in tension or flexion without proper steel reinforcements. The mechanical strength of concretes depends on the stability of hydrated cement matrix as well as on the stability of the transition zones, i.e. the interfaces between aggregates (gravels/sands) and the matrix. It is the hydrated cement matrix that creates a rigid binding skeleton combining all the hydration products and aggregates.

The mechanical strength of the cement matrix formed from hydrated cement paste is strongly influenced by its *porosity* P, calculated as the ratio of the volume of the pores to the total volume of the material. The diameters of pores range from the nanometric region (tiny gel pores; ~ 0.1 nm, ~10 nm) up to micrometric region (capillary pores; ~0.1 μ m, ~10 nm). A special group of air voids (≥ 1 mm) may or may not appear during preparation or curing of cement paste. These air voids are not a result of hydration reactions; rather they result from imperfect technological procedures during mixing of cement grains with water. Thus they are not an inherent part of the structural porosity. It is well-known that *capillary pores (spaces between cement grains)* in particular influence both the compressive and the tensile/flexural strength. A higher portion of capillary porosity leads to lower mechanical strength of the cement paste.

2. Relations for mechanical strength

There are many analytical expressions for compression strength [1] in which porosity P is a decisive factor. However, there are only a few such expressions [2-5] for flexural (bending) strength. One of those few expressions of flexural strength was derived [2] in a quite general form that can be adjusted for cement pastes as follows:

$$\sigma_{por}^{(flex)} = \sigma_o \sqrt{(1 - \frac{P}{P_c})^\beta \cdot (1 - P^{2/3})}, \quad 0 \le P \le P_c \tag{1}$$

where σ_o is maximum strength at zero porosity ($P = 0$), the exponent β is a parameter that has to be optimized for the particular material, and P_c is a critical porosity for which the flexural strength approaches zero $\sigma_{por}^{(flex)}(P = P_c) = 0$. In practice, the symbols β and P_c are fitting parameters.

In contrast to porous materials, there are materials like glassy ones that have *zero porosity*. According to Griffith [6], the structural *single macrodefects* embedded in the volumes of such non-porous materials play a decisive role in the *flexural strength*. For *non-porous brittle materials*, Griffith [6] derived a formula that estimates flexural strength by means of the Young's modulus of elasticity E, the fracture surface energy 2γ, and the radius r of a single critical *macrodefect*:

$$\sigma_{mdef}^{(flex)} = \sqrt{\frac{2\gamma E}{\pi r}} \tag{2}$$

The Griffith fracture criterion (2) was originally derived for ideally brittle materials, but Birchall et al. [7] showed that it may also be applicable to *quasi-brittle Portland cement paste,* which is otherwise a *highly porous* material. This curious situation when highly porous material is tested by using the Griffith criterion (2) originally designated for non-porous materials containing only one macrodefect (or a limited number of macrodefects) poses a relevant question concerning the conditions under which the Griffith criterion may show correct results even with porous materials. This computational dilemma has a seemingly easy solution. The Griffith criterion may be applicable to porous materials if the Griffith flexural strength (2) is lower than the 'porous' strength (1), that is,

$$\sigma_{mdef}^{(flex)} \le \sigma_{por}^{(flex)} \tag{3}$$

On the basis of equations (1) - (3) the radius r_c of a *critical macrodefect* can be deduced for each value of porosity associated with the particular material:

$$r_c \ge \frac{2\gamma E}{\pi \sigma_0^2 [(1 - \frac{P}{P_c})^\beta \cdot (1 - P^{2/3})]} \tag{4}$$

When introducing into a porous material an artificial macrodefect whose radius r is greater than the critical one, $r \ge r_c$, the flexural strength will be governed by the Griffith criterion (2). This was experimentally shown by Birchall et al. [7] with ordinary Portland cement paste. These authors introduced notches of various depths into the cement specimens and measured their flexural strength in three-point bending tests. The specimens with very deep notches fulfilled the Griffith criterion (2) but as soon as the value of the depth of notches fell under the critical limit of ~1.1 mm, the Griffiths strength ceased functioning and a normal 'porous' strength stabilized.

The presence of defects whose radii are smaller than the critical radius, $r < r_c$, will not dominantly affect the flexural strength, and in this case the strength will be governed by porosity, that is, by the collective action of all pores. Similarly, if the radii of the largest capillary pores are smaller than the

critical radius r_c, they will not cause the Griffith weakening of the structure but again it will be the capillary porosity that will be decisive.

Why cannot the largest *under-critical* capillary pores ($r < r_c$) cause Griffith weakening and why does porosity dominate? Why do the small capillary pores influence the flexural strength equally as well as or even more than the largest pores in these cases? To explain the essence of collective action of pores, let us discuss an *idealized model of material structure* whose porosity P is formed by pores of *identical radii* r. If a homogeneous material contains only a few such defects, the corresponding porosity is extremely small, that is, close to *zero* ($P \to 0$), and according to equation (4) the critical radius r_c is given exactly by the Griffith criterion (2), in which the flexural strength σ_o is associated with the homogeneous *non-porous* structure. These several defects (pores) play the role of the Griffith macrodefects provided that their radius r is comparable with or larger than r_c.

On the other hand, if the number of these uniform pores is huge, the porosity is very large, approaching the value of P_c ($P \to P_c$), and according to equation (4) the critical radius r_c increases massively ($r_c \to \infty$). As a consequence, r_c is much larger than r, and thus the flexural strength cannot be governed by the Griffith criterion but is instead governed by porosity, that is, by the collective action of all these uniform pores. Their huge number ensures that the *average thickness of the walls between pores is quite small* and this is the reason why the material structure is weakened. The larger the number of pores, the thinner the walls and the lower the mechanical strength. This is the essence of the collective action of *pore microdefects* in contrast to the individual action of the *single macrodefects*, whose restricted number cannot influence the average thickness of the inter-pore walls sufficiently. This is the interplay between micro- and macrodefects within porous materials.

As to the collective action of capillary pores with cement pastes, the situation is a little different. The spaces between cement grains (capillary pores) are partly filled with the fibers of calcium silicate hydrates (so-called C-S-H gel). The fibers are mutually interwoven and mutually bound. It is well-known that a higher water-to-cement ratio (w/c) of the cement paste leads to higher porosity and lower mechanical strength of this material. A higher portion of water causes larger inter-grain distances (larger capillary pores) in which the C-S-H fibers are *loosely packed (weakly bound)* and this causes a *lower mechanical strength*. An increase of the inter-grain spaces does not automatically mean that the largest capillary pores (r_{max}) may exceed the critical radius r_c. The huge number of pores ensures a high porosity, which guarantees a sufficiently high value of r_c ($r_c > r_{max}$). In addition, it was shown that the largest pores in the spectrum of capillary pores change their sizes negligibly [8]. In such cases, the increase in total porosity is caused by the cumulative increase of all capillary pores. Finally, the importance of the mechanical strength of the inter-grain bonds implemented by C-S-H fibers was also highlighted by Higgins and Bailey [9].

3. Experimental arrangements

To illustrate experimentally some characteristic features of flexural strength and critical radius r_c, a large set of 70 specimens made of ordinary Portland cement pastes were tested. The specimens had been hydrated under standard conditions for 3 years. They were divided into seven groups according to their water-to-cement ratios (*w/c* = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8). Each group contained 10 specimens. The porosity of each group of specimens was measured by the gravimetric method (P = 0.209, 0.272, 0.337, 0.388, 0.473, 0.526, and 0.5852). The specimens were subjected to three-point bending tests to estimate their values of fracture energy (2γ), Young's modulus of elasticity (E), and flexural strength σ

$$2\gamma = \frac{\displaystyle\int_{0}^{y_{max}} F(y)\,dy}{S} \quad (\text{J/m}^2), \quad S \approx h \times H \quad (\text{m}^2) \tag{5}$$

$$E = \frac{L^3}{4hH^3\alpha} \quad (\text{Pa}), \quad \alpha = \frac{\Delta y}{\Delta F} \quad (\text{m/N}) \tag{6}$$

$$\sigma = \frac{3F_{max}L}{2hH^2} \quad (\text{Pa}) \tag{7}$$

where S is a cross-sectional area of specimens, F loading force and $L = 6.4$ cm is a distance between two supports of the testing apparatus (see figure 1). The weights of the used small specimens did not exceed 2.5 N. These values are negligible in comparison with the loading forces F reaching hundreds of Newton and thus the weights of specimens were not included into equations (5) - (7).
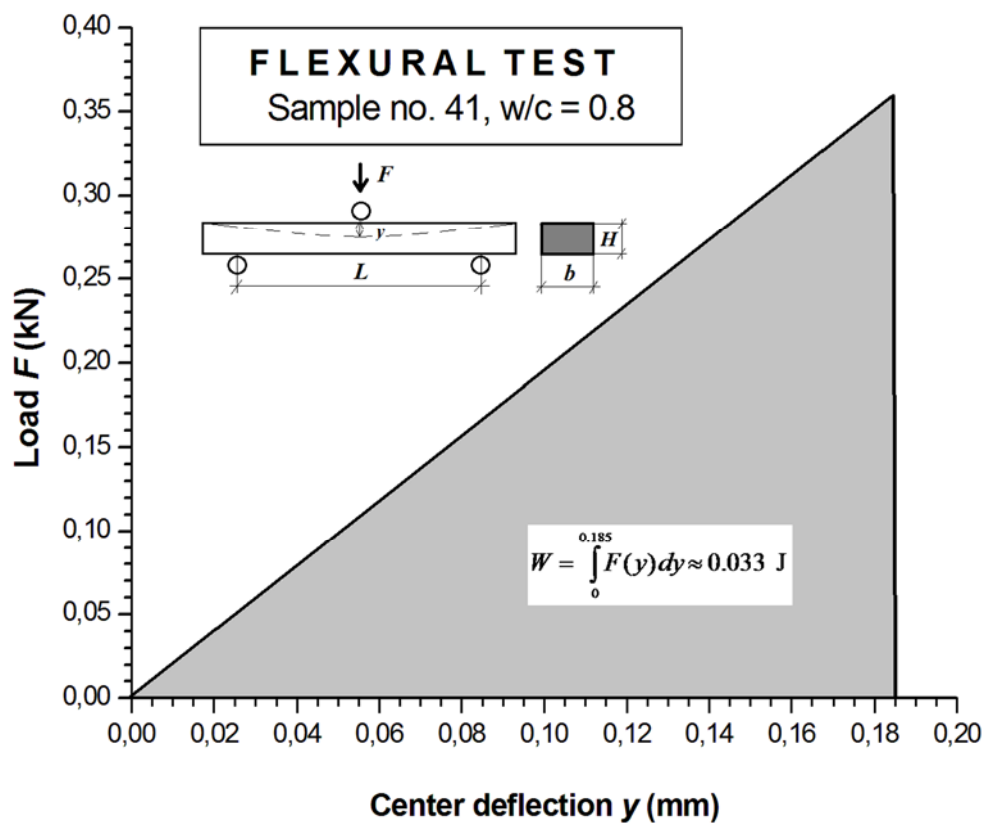

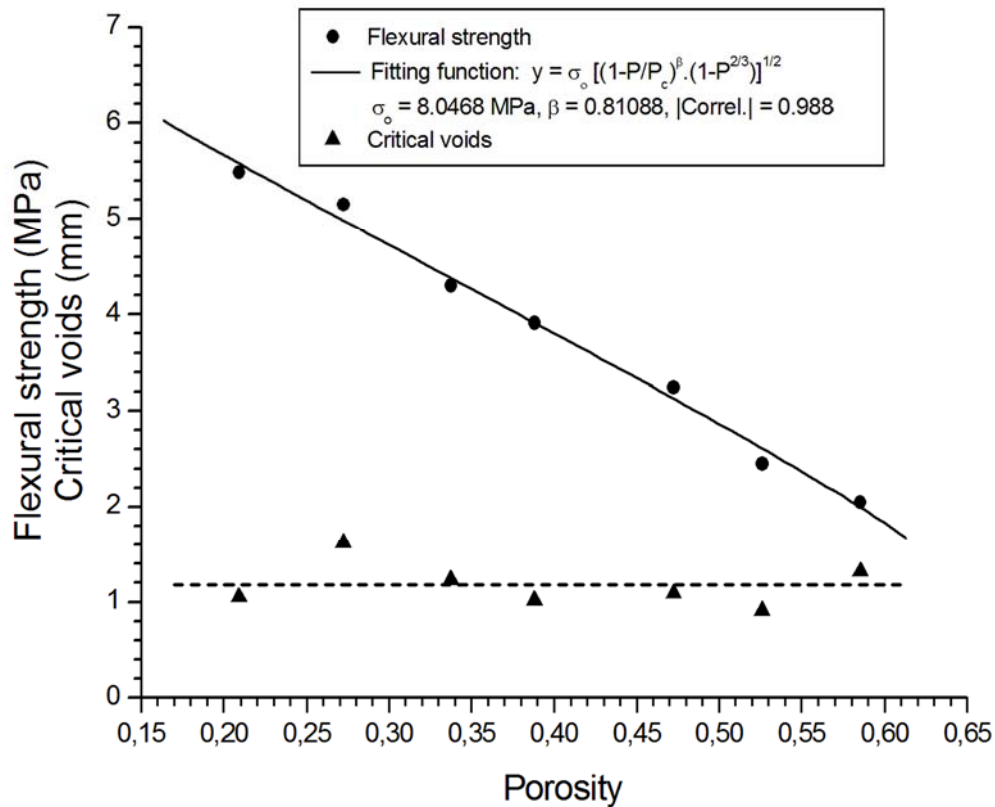**Figure 1.** Flexural test and fracture work

Figure 2. Results of the flexural tests of ordinary Portland cement pastes

4. Results and discussions

The measured values of 2γ, E and σ together with the porosities P enabled us to calculate the *average* critical radius r_c for each group of specimens according to equation (4). The graph $r_c(P)$ along with the graph of the measured flexural strength can be inspected in figure 2.

The graph of the measured flexural strength in figure 2 shows a clear dependence on porosity. There are no symptoms indicating the Griffith weakening of the structure. The critical radii r_c of the specimens assume an almost uniform value of $r_c \approx 1.18$ mm, marked by the horizontal dashed line in figure 2. This value is identical to that found by Birchall et al [7] when they analyzed the influence of macrodefects on the flexural strength of ordinary Portland paste. The Griffith flexural strength of their notched specimens converged to normal 'porous' strength as soon as the size of macrodefects (depth of notches) approached the value of $r_c \approx 1.1$ mm. The results obtained by these authors concerned only single porosity, that is, a single water-to-cement ratio of $w/c \approx 0.2$. For this reason, they could not report on pastes of different porosities and, as a consequence, their report remained incomplete and missed the core problem concerning the roles of macro- and microdefects in the mechanical strength of porous materials.

The results of the complete analysis discussed in the present paper include a wide range of porosities, which enabled us to shed light on the problem of macro- and microdefects in porous materials and to

reveal *surprising features of the critical radii* r_c of hydrated cement pastes. As seen in figure 1, the critical radius r_c of cement pastes assumes a uniform value of ~1.18 mm irrespective of the actual values of porosities and simultaneously corresponds to the Griffith critical flaw of the 'ideal' *non-porous structure* of cement paste. This result is only seemingly in contradiction to equation (4), because porosity P influences not only the denominator of fraction (4) but also its numerator, that is, $2\gamma(P)E(P)$. Such a *paradoxical result* showing *uniformity of critical radii* irrespective of porosity is undoubtedly connected with the fact that natural capillary pores themselves cannot change the radius of the Griffith critical flaw, which is associated with the *'parent'* <u>poreless</u> *substance*, whose *inherent properties* are independent of the pore spaces themselves. Since cementitious materials do not represent a special group among other porous materials and even share many common features with them, the *uniformity of critical radii* as a real property of many other porous materials cannot be excluded.

5. Conclusions

It has been shown that the mechanical strength of cement matrix (hydrated cement paste) is a result of competitive interplay between macrodefects and microdefects. The dominance of one of these two kinds of defects depends not only on their sizes but also on their numbers. The cross-over between dominances of macrodefects or microdefects is determined both by a critical number of defects and by their critical size.

The critical radius r_c of cement pastes assumes a uniform value of ~1.18 mm irrespective of the actual values of porosities and simultaneously corresponds to the Griffith critical flaw of the 'ideal' *non-porous structure* of cement paste.

Since cementitious materials share many common features with other porous materials, their uniformity of critical radii might also be expected with some other porous materials.

Acknowledgment

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