# A capillary action test for the investigation of adhesion in repair technology

## Luc Courard and Robert Degeimbre

**Abstract:** When repair material is laid down on a concrete substrate, the porosity of concrete allows it to penetrate the substrate, increasing the probability of physical interactions, and subsequently increasing adhesion. Water absorption by immersion or usual capillary action tests do not provide enough information to understand what happens when contact occurs between the concrete substrate and the cement slurries used as a bonding layer. An adaptation of the capillary action test is presented; this is based on a continuous measurement of mass change of the sample. Major differences according to the type of surface preparation are pointed out: absorption rates as well as mass changes are greater for polished concrete substrates than for sandblasted ones. Centrifuged solutions of cement slurries modified with plasticizers and superplasticizers are used for water replacement in the adapted capillary action test. Results clearly show the influence of these admixtures: the greater the adhesion tension, the greater the wetting of the concrete substrate. Determination of these thermodynamic characteristics and performance of an adapted capillary action test provide a better understanding of the mechanisms of interface creation and promotion of adhesion.

*Key words:* concrete, substrate, repair, capillary, absorption, impregnation, interface, centrifugation, superficial tension, pore radius.

**Résumé :** Lorsqu'un matériau de réparation est appliqué sur un support en béton, il va pénétrer dans le béton, favorisant par là-même l'adhésion en augmentant la probabilité d'occurrence des sites d'interaction physique. Le phénomène de succion capillaire et la porosité du support sont à la base de ce mécanisme. Les essais classiques d'absorption d'eau par immersion et par capillarité ne rendent pas suffisament compte de ce phénomène. Une adaptatation de l'essai d'absorption capillaire assurant un enregistrement continu de la quantité de liquide absorbée est présentée. Les résultats permettent de montrer une différence de comportement, dès la mise en contact, en fonction du type de préparation de surface : la vitesse d'absorption et la quantité d'eau absorbée sont plus importantes pour les surfaces polies que pour les surfaces sablées. Des solutions centrifugées de barbotines de ciment, modifiées avec plusieurs plastifiants et superplastifiants, sont utilisées à la place d'eau dans le cadre de l'essai adapté d'absorption par capillarité. Les résultats mettent clairement en évidence l'influence de la tension d'adhésion, qui doit être la plus grande possible. La détermination de ces caractéristiques thermodynamiques et physiques, couplée à la réalisation de ce nouvel essai, permet d'avoir une meilleure vue du mécanisme à la base de la création de l'interface.

*Mots clés :* béton, support, réparations, capillarité, absorption, imprégnation, interface, centrifugation, tension superficielle, rayon poreux.

## 1. Introduction

Cement slurries are often used as bond coats between the old concrete substrate and the new repair material. Transfer phenomena at the interface between the concrete substrate

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and these slurries are dependant on the internal structure of the substrate and characteristics of the applied slurry (Mindess 1987). Characteristics such as viscosity, shear level, and surface free energy should be studied (Tabor 1981). Ion transfer depends on both concentration gradients and electric forces and generally occurs in a homogeneous medium through a liquid phase (Kinloch 1987). Liquid and gas movements depend mainly on pressure differences and capillary suction (Courard and Darimont 1998). Pressure difference assumes a pressure gradient between the surface and the bulk concrete, which is very unlikely in concrete repair scenarios, since pressure difference can be derived only from the forces applied during the application of the repair material and its associated weight. These forces are usually not more than 40 to 50 Pa (Courard 1999).

Capillary suction causes the transfer of liquids into porous solids (Justnes 1995), mainly because of the interfacial tension between the liquid and solid phases. This is on the basis

of material durability (Wirquin et al. 2000) because capillary pressure is the "driving force" of the transfer phenomenon. It will cause the penetration of water and usually ions from the surrounding environment into the concrete structure. This is also an important mechanism for concrete repair, which relies on the properties of the interface zone between the repair material and the concrete substrate. It can regulate the transfer of water from the repair material to the substrate, especially when the latter is dry. This transfer will modify both the cement setting process and the development of adhesion at the interface.

Capillary suction is a continuous and important phenomenon (Sabir et al. 1998). An understanding of the liquid exchange velocity (Wirquin et al. 2000) and a superficial porous skeleton of the concrete substrate is essential. Its behavior will depend on the shape and the dimensions of the capillaries present.

This work presents an original way to understand relationship between capillary action and adhesion in repair technology. It is based on the development of a special test, named "online" capillary absorption, which instantly shows the capillary rate. This test is compared with the classical capillary suction test. Interstitial solutions of cement slurries as well as water are studied to more accurately simulate the absorption process after contact with the concrete substrate.

## 2. Theoretical basis

A good bond between a concrete substrate and a repair material, i.e., a cement slurry in this study, requires that the latter be of sufficiently low viscosity to spread on the surface and penetrate into the capillaries. Contact must occur as soon as possible, because viscosity of the repair material increases with time because of the hardening process and the evaporation of the liquid phase. Capillary action, one of the main phenomena in creating contact, is governed by Laplace's law (Jouenne 1980). This defines the increase of hydrostatic pressure $p_a - p_w$ as a function of superficial tension of the liquid $\gamma_L$ and average curvature of the liquid meniscus $1/R$, where $p_a$ is the atmospheric pressure and $p_w$ is the water pressure.

When the capillary radius can be considered as sufficiently short to assimilate the meniscus surface as a half-sphere with radius $r$ (Fig. 1), we have

$$[1] \qquad p_a - p_w = \frac{2\gamma_L \cos\theta}{r}$$

where $\gamma_L$ is the surface free energy of liquid and $\theta$ is the contact angle.

The height of capillary movement $H$ can be evaluated from Jurin's law (Jouenne 1980; Beiser 1978)

$$[2] \qquad H = \frac{2\gamma_L \cos\theta}{pgr}$$

where $p$ is the capillary pressure and $g$ the acceleration of gravity.

For a horizontal capillary for which one end is in contact with air and the other with water, we can write the flow of liquid on the basis of Poiseuille's law (Jouenne 1980).

When the liquid attempts a distance $x$, we can write

Fig. 1. Capillary action when solid surface is partially wetted by liquid phase ($\theta < 90°$).
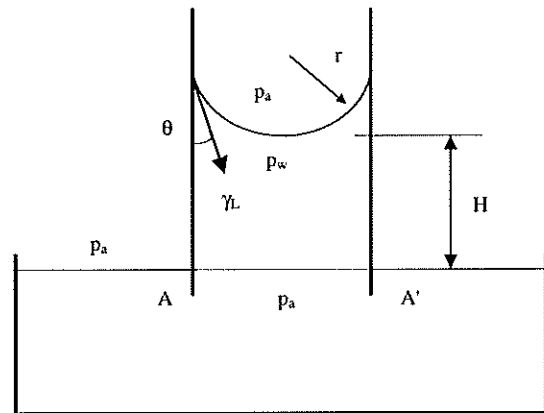


$$[3] \qquad Q = \frac{\pi p r^4}{8\eta x}$$

where $Q$ is the flow of liquid and $\eta$ is the viscosity of the liquid.

By integrating change of volume $dV$ ($dV = r^2\, dx$) with time $dt$ and considering $\theta$ and $\eta$ constants (usually meaning constant temperature), Washburn's equation (Kinloch 1987) gives the change of penetration height of a liquid into a capillary as the square root of time and radius

$$[4] \qquad l_p = \sqrt{\left(\frac{r\gamma_L \cos\theta}{2\eta}\right) t}$$

where $l_p$ is the change of the penetration height of the liquid, $r$ is the radius of the pore, and $t$ is time.

If we assume a porous material to have a large number of capillaries parallel to each other, with different diameters and perpendicular to the surface of the liquid, the liquid will be absorbed with a higher force by the shorter capillaries, according to Laplace (Jouenne 1980), but faster and in large quantities by the largest pores, according to Washburn (Courard 2000).

Other interesting information can be deduced from Washburn's equation (Derjagin et al. 1978). Higher penetration will be observed when (i) viscosity of the liquid decreases, (ii) surface free energy of the liquid increases, and (iii) contact angle is close to zero.

The last two conditions are inconsistent (Courard 1999) and a compromise must be found. For a defined concrete surface, it can be achieved by selecting a liquid characterized by a surface free energy $\gamma_L$, just below the critical surface tension of wetting $\gamma_c$ (Kinloch 1987; Courard 2002). Another interesting observation can be made with regard to Washburn's equation. Until now only cylindrical pores have been considered where for low values of $\theta$, penetration height $l_p$ is high. However, $l_p$ quickly decreases with increase of $\theta$ (Fig. 2). The behavior is quite different for "ink-bottle" pores, where penetration is limited and rapidly becomes zero. The influence of the pore entry is clearly observed here and will influence the penetration rate.

Fig. 2. Comparison of the penetration of a liquid into cylindrical and "ink-bottle" pores (Kinloch 1987).



Fig. 3. Influence of capillary mouth shape.
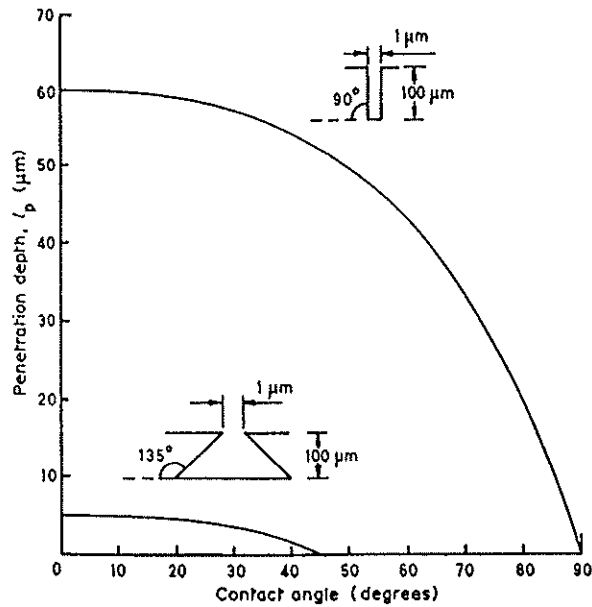


Again, it can be observed (Fig. 3) that pores similar to those in Fig. 3b are not favorable to water penetration, compared with pores in Figs. 3a and 3c.

Analysis of mercury intrusion porosimetry (MIP) and nitrogen adsorption isotherms is based on pore shape, i.e., cylindrical, ink-bottle. (Lecloux 1981). They concern low-radius capillaries, i.e., between 2 nm and 75 μm, unable to absorb large quantities of water in a short period of time (Courard 1999). These techniques could, however, provide information about the influence of the capillary entry on penetration rate, and MIP will be used for this purpose.

Consequently, the potential effect of capillary entry shape on capillary action in repair techniques needs to be simultaneously analyzed by means of MIP and classical absorption tests. These types of tests include the coarse pores and will therefore influence liquid transfers.

Capillary action test methods as a means to investigate interfacial movements and interactions are presented in the following sections.
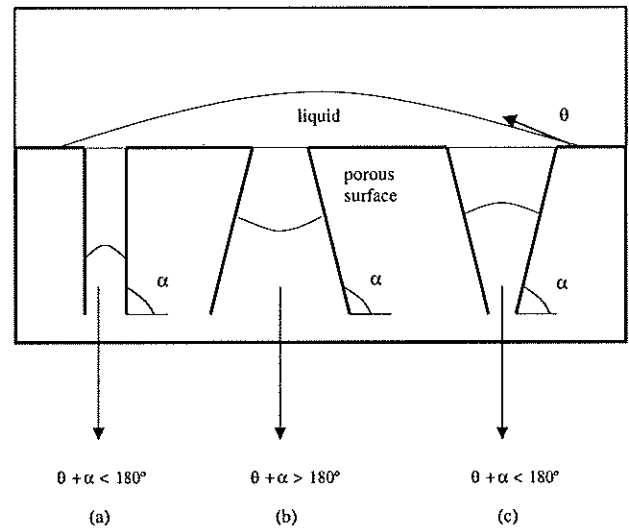
## 3. Experimental works

### 3.1. Description of materials

Concrete slabs (100 cm × 50 cm × 5 cm) were made; the concrete mix was designed with 2/8 mm limestone aggregates, 0/2 and 0/5 mm sands and cement with fly ashes (CEM II B-M 32.5); water–cement (w/c) ratio was fixed at 0.5. Slabs were stored in standardized curing conditions (28 d at 20 °C and 100% relative humidity before surface preparation.

Half of the slabs were sandblasted and the other half polished. The samples were sandblasted with sand 1/1.4 mm, with more than 65% corundum (95.1% $Al_2O_3$ and 0.1% $Fe_2O_3$) projected on a form-worked surface. Polished samples were obtained by means of two abrasive and rotating

wearing plates, and samples were polished until the surfaces were "smooth to the touch" (Courard 1998). All slabs were cleaned with pressurized water after preparation.

The limestone specimens were prepared with a diamond saw; the rock was the same as the aggregates used for concrete slab preparation.

Cement slurries were applied by brushing onto the different slabs. Based on a mix of Portland cement CEM I 42.5 and a w/c ratio of 0.4, they were modified with admixtures to optimize contact and penetration into the concrete substrate (Table 1). An admixture is characterized by its main component. Reference VII corresponds to pure cement slurry.

Slurries were applied on dry 90-d-old concrete slabs. Just before application, they were dried for 24 h at 105 °C and stored for 7 d at 23 ± 2 °C and 50 ± 5% relative humidity. After application, recovered slabs were stored for 28 d at 23 ± 2 °C and 100% relative humidity.

### 3.2. Measurement of adhesion strength

Adhesion strength was measured by direct tensile test according to Belgian standard NBN B15-211 (1974). Specimens of 5 cm diameter (surface area 1964 mm²) were cored in different slabs covered with slurries. Specimens were glued with epoxy resins on steel discs to be fixed in a tensile laboratory test machine. The load was applied continuously and uniformly at a speed of 0.1 ± 0.05 MPa/s. Both adhesion strength and rupture type are deduced (Courard 1999).

### 3.3. Water immersion

Physical properties are fundamental to understand transfer mechanisms at the interface. Porosity, impregnation ratio, and water absorption are all important to correctly define the superficial layer of concrete substrate. Open porosity is defined as the ratio between specific volume and water absorption, and accessible porosity as the ratio between specific volume and water absorption under vacuum.

This first type of test implies total immersion in water to the concrete sample (NBN B15-215 1969). Water comes into

Table 1. Admixtures used for cement slurries.

| Reference | Product | Viscosity (mPa·s) Cement slurry | Viscosity (mPa·s) Centrifuged solution |
|---|---|---|---|
| I | Melamine | 309 | 1.412 |
| II | Melamine | 670 | 1.463 |
| III | Napthalen | 434 | 1.587 |
| IV | Vinyl copolymer | 474 | 1.464 |
| V | Maleic acid | 486 | 1.366 |
| VI | Natrium ligno-sulfate | 1186 | 1.389 |
| VII | No admixture (pure paste) | 1389 | 1.518 |

the sample from the six faces of the cubes, independent of the quality of the surface in relation with the repair material. This is a "bulk test" that gives a global value of porosity.

### 3.4. Capillary suction coefficient

The most commonly used test to analyze water transfer at the interface is the capillary suction test (Courard 1999; Justnes 1995). The capillary suction test is described by several standards around the world, namely, NBN B14-201 (1973), DIN 52617 (1987), prEN 13057 (2000), prEN 480-5 (1996), which differ essentially by the water level above the bottom surface of a concrete specimen and the time when measurement is taken. Mass change is usually measured after 5, 15, 30, and 45 min, as well as after 2, 6, and 24 h. Mass is measured on samples wiped off with a damp tissue.

From the capillary suction test it is possible to calculate the rate of water absorbed by the capillaries ($E_c$, %) and the water absorbed under vacuum ($E_v$, %). One can then calculate the relative impregnation ratio $S_t$, at time $t_i$
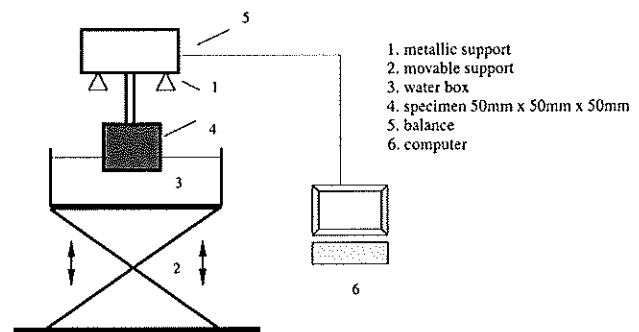
$$[5] \qquad S_t = \left(\frac{E_c}{E_v}\right) 100$$

This value is characteristic of the absorption rate of the substrate at any time versus a complete filling of the porous skeleton (corresponding to accessible porosity of concrete samples).

### 3.5. Online capillary absorption

Capillary forces exist when contact is made between the concrete substrate and the repair system. The liquid phase wets the solid surface and goes up into the capillaries. A new test was developed to continuously measure mass change of the specimen during capillary action (Fig. 4).

Specimens are cubes from 45 to 50 mm in length with lateral faces (five out of six) coated with an epoxy resin to avoid lateral penetration and (or) evaporation of water as shown in Fig. 4. Water comes up from the bottom until contact is made with the sample. The immersion height can be altered. Mass change was continuously monitored (1 or 5 s), and the measurements obtained from a balance were saved through the application of appropriate computer software (Figs. 4 and 5). The entire test device is protected from wind and any other interference by a plexiglass box.

Fig. 4. Continuous capillary suction test scheme (Courard and Darimont 1998).



1. metallic support
2. movable support
3. water box
4. specimen 50mm x 50mm x 50mm
5. balance
6. computer

### 3.6. Mercury intrusion porosimetry

A confirmation of the influence of capillary entry shape or capillary absorption could come from the analysis of the internal skeleton of the concrete. Only superficial concrete (5 ± 1 mm) is analyzed, as it will be influenced principally by liquid movements. Mercury intrusion porosimetry (2000 bars) gives a granulometric gradation of the pores between 7.5 nm and 75 µm, as well as evaluation of specific surface, total porous volume, and mean radius.

### 3.7. Capillary suction of cementitious products

Investigations have been realized until now on pure water to point out the effects of capillary shapes and entries of substrate materials. In the reality of repair techniques, water is modified by cementitious materials, admixtures, and (or) additions. This could modify absorption capacity of solid materials because of change in viscosity, surface free energy, or presence of particles in suspension in the liquid phase.

Cement slurries modified with admixtures have been prepared, but because we observed that only the interstitial phase was able to penetrate into the concrete substrate (Courard and Darimont 1998), we decided to use only the liquid phase obtained in accordance with the specific procedure:

• mix water and cement CEM I 42.5 (w/c = 0.5) for 3 min and divide the mixture into four parts to fill the containers of a Sorval centrifugation device
• centrifuge for 20 min at 6000 rounds per minute
• collect the centrifuged solutions (±100 mL) into containers after filtration with Wathman paper no. 51 (retention of 20–25 µm particles).

It is mainly this part of the slurry that will be able to penetrate into superficial porosity of concrete because of the relatively small dimension of cement particles and pore radius.

Theoretical viscosity of water is 1 mPa·s ($T = 20$ °C). Therefore, we can consider that viscosity of the centrifuged solutions is the same as that of water.

A test similar to that described in Sect. 3.5 was performed on polished concrete slab samples. Capillary suction as a function of time was first monitored with water (samples ref. PXw) and, secondly, after drying at 105 °C until constant mass, with one centrifuged solution (samples ref. PXc), with X corresponding to the different modified cement slurries (Table 9).

Fig. 5. Measuring and registering device system (Baudoin 1997).
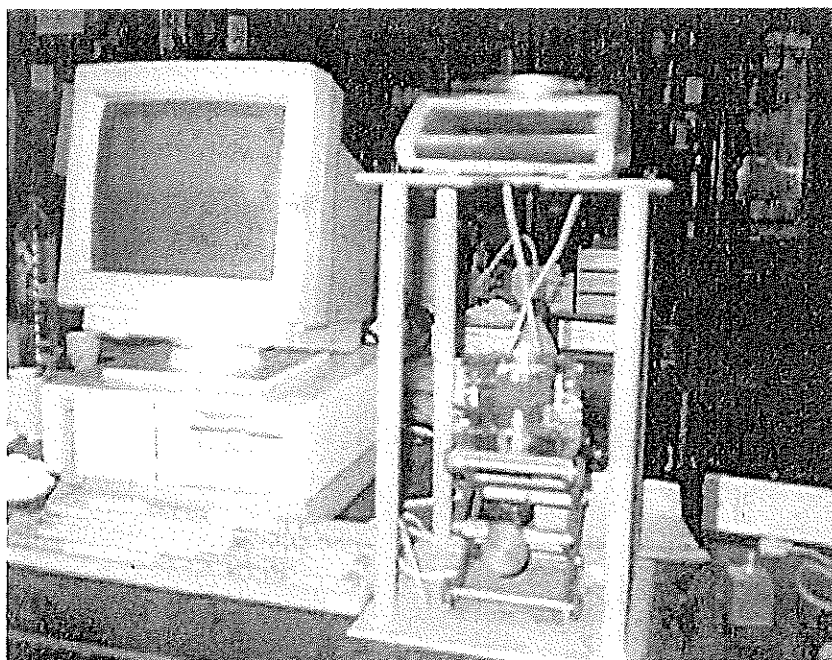


## 4. Results and discussion of the tests

### 4.1. Mechanical characteristics and adhesion strength

The compressive strength of a 50-mm-diameter core was 55.6 MPa (standard deviation 11.2%) and 4.16 MPa in traction (standard deviation 15%). This last test is realized by means of a pull-off test without sawing or coring (EN 1766 1995). The specific volume is given as 2.22 g/cm$^3$ (standard deviation 1.35%). Specific volume of limestone is 2.68 g/cm$^3$.

Table 2 gives the results of adhesion strength for a minimum of five specimens by combination. Almost all types of rupture shapes are cohesive rupture in the concrete substrate. This means that adhesion is at least the mean value given in Table 2.

Analysis of results indicates that for five out of seven slurries, polished concrete surfaces show an adhesion better than that of sandblasted samples. Consequently, since it appears that, in this study, adhesion is better on smoother concrete surfaces, roughness is clearly not the only parameter to be taken into account. Specific adhesion must be explained also by differential penetration depths of slurries.

### 4.2. Water immersion and capillary suction coefficients

Water immersion test results (Table 3) clearly indicate that the concrete substrates have the same behavior independent of the surface preparation. Open and accessible porosity can be deduced from specific volume and Table 3 (Table 4). They are relatively high, because of the mix design and the discontinuous granulometry of aggregates.

Figure 6 gives results of capillary suction on cubes 5 cm in length immersed in water on 5 ± 1 mm high (DIN 52617 1987); mass change is measured after 5, 15, 30, and 45 min as well as after 2, 6, and 24 h. Three samples of each cate-

Table 2. Adhesion of cement slurry on sandblasted and polished concrete substrates.

| Modified cement slurry | Adhesion (MPa) | |
| --- | --- | --- |
| | Sandblasted concrete substrate | Polished concrete substrate |
| I | 3.09 | 2.89 |
| II | 3.66 | 3.67 |
| III | 3.25 | 2.76 |
| IV | 2.45 | 4.19 |
| V | 2.82 | 3.86 |
| VI | 2.65 | 3.26 |
| VII | 2.76 | 4.09 |

Table 3. Water absorption on concrete substrates.

| Sample | Water absorption (%) | Water absorption under vacuum (%) |
| --- | --- | --- |
| Sandblasted concrete slab | 5.49 | 8.99 |
| Polished concrete slab | 5.38 | 8.59 |
| Limestone | 0.27 | 0.29 |

Table 4. Open and accessible porosity of concrete substrates and limestone.

| Sample | Open porosity (% in volume) | Accessible porosity (% in volume) |
| --- | --- | --- |
| Sandblasted concrete slab | 12.19 | 19.96 |
| Polished concrete slab | 11.94 | 19.07 |
| Limestone | 0.72 | 0.78 |

**Fig. 6.** Water absorption by capillary suction according to the German standard DIN 52617 (mass variation in grams; S, sandblasted; P, polished concrete; R, limestone rock).
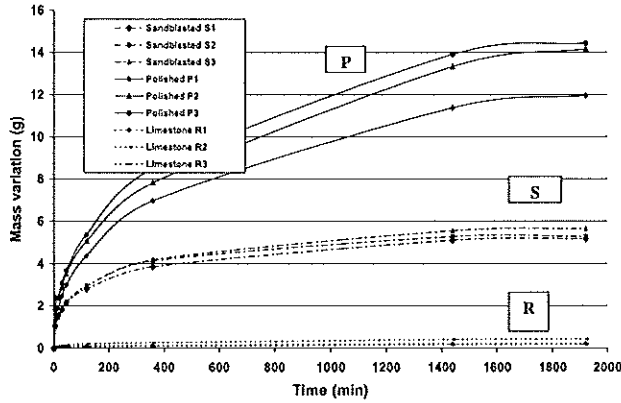


**Fig. 7.** Mass change on samples of sandblasted concrete, polished concrete, and limestone between (*a*) 0 and 60 s and (*b*) 0 and 2400 s.



**Table 5.** Relative impregnation ratio ($S_t$) for sandblasted concrete slabs, polished concrete slabs, and limestone (change in %).

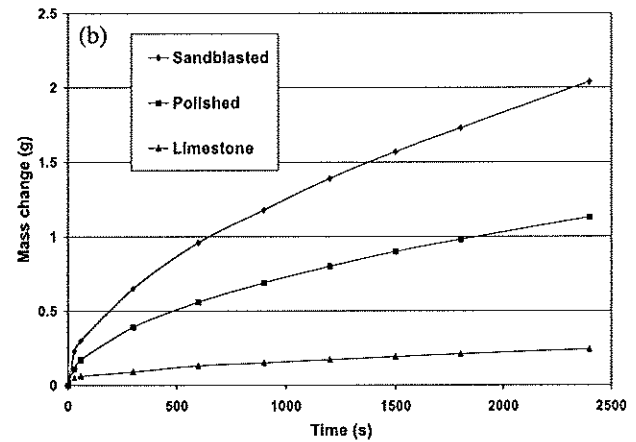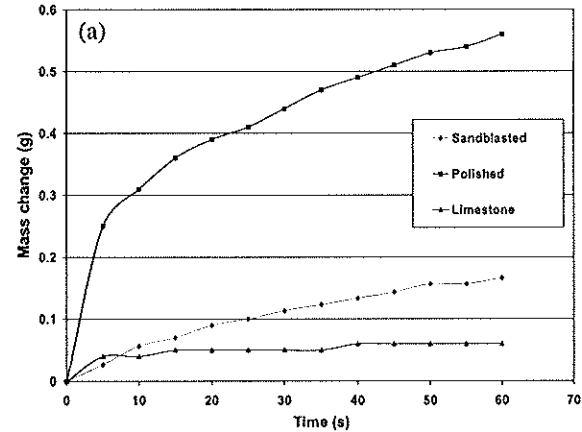| Time (min) | Relative impregnation ratio $S_t$ (%) | | |
|---|---|---|---|
| | Sandblasted concrete slabs | Polished concrete slabs | Limestone |
| 5 | 7.3 | 9.43 | 10.36 |
| 10 | 7.96 | 12.92 | 14.90 |
| 15 | 8.61 | 15.25 | 15.67 |
| 30 | 11.06 | 18.86 | 17.99 |
| 45 | 13.34 | 21.54 | 19.84 |
| 60 | 14.89 | 24.21 | 21.68 |
| 120 | 19.34 | 30.73 | 29.17 |
| 180 | 22.14 | 35.39 | 32.54 |
| 360 | 30.53 | 40.92 | 42.65 |
| 1440 | 50.61 | 57.51 | 58.90 |

gory (S for sandblasted concrete, P for polished concrete, and R for limestone rock) have been tested. From Fig. 6, one can calculate the rate of water absorption (Table 5). This result shows that the polished specimens seem to absorb higher quantities of water by capillary action than the sandblasted ones. This phenomenon is observed throughout all three tested specimens (P1 to P3). Observation of the curves indicates that the differences are most significant at the beginning of the test. After some time, absorption speed levels off and then remains constant.

The reasons for the differences in absorption rate could be (*i*) shape of pore entries and capillaries, (*ii*) granulometry of pores at the surface, (*iii*) presence of a pollutant, (*iv*) difference in carbonation depth that could reduce pore diameter, and (*v*) air bubbles.

Moreover, we observe a similar relative impregnation ratio $S_t$ for polished concrete and limestone. This indicates that the cement paste and the interfacial transition zone around the aggregates are filled as quickly as the porous skeleton of limestone, even if the pore volume and skeleton granulometry are not the same.

These observations clearly show the need for developing a suitable test to investigate and measure capillary absorption from the beginning. In the present study (Figs. 4 and 5), water capillary action was monitored on sandblasted and polished concrete samples and limestone bulk material. Figure 7 presents the results of mass change between 0 and 60 s and between 0 and 2400 s on different samples. Mean values are based on three specimens for sandblasted concrete, eight for polished concrete, and three for limestone.

Statistical analysis based on comparison of absorption curves by nonlinear regression confirms a difference in the behavior of the three types of substrates.

The values of relative impregnation ratio $S_t$ (Table 6) exhibit a difference between sandblasted and polished samples. The value of $S_t$ for polished concrete is generally twice that of sandblasted samples.

Since the open and accessible porosities for the two concrete substrates are the same, the differences can come only from the shape of the pores at the surface. The carbonation and pollution hypothesis can be dismissed because of the care taken in sample preparation. The coating used in the

**Table 6.** Relative impregnation ratio ($S_i$) on sandblasted concrete slabs, polished concrete slabs, and limestone (change in %).

| Time (s) | Relative impregnation ratio $S_i$ (%) | | |
|---|---|---|---|
| | Sandblasted concrete slabs | Polished concrete slabs | Limestone |
| 5 | 0.22 | 2.03 | 9.05 |
| 10 | 0.48 | 2.70 | 9.05 |
| 15 | 0.59 | 3.11 | 11.31 |
| 20 | 0.76 | 3.39 | 11.31 |
| 25 | 0.84 | 3.63 | 11.31 |
| 30 | 0.95 | 3.83 | 11.31 |
| 35 | 1.04 | 4.06 | 11.31 |
| 40 | 1.12 | 4.27 | 13.58 |
| 45 | 1.21 | 4.41 | 13.58 |
| 50 | 1.32 | 4.59 | 13.58 |
| 55 | 1.32 | 4.69 | 13.58 |
| 60 | 1.40 | 4.84 | 13.58 |
| 300 | 3.34 | 9.41 | 20.37 |
| 600 | 4.67 | 13.23 | 29.42 |
| 900 | 5.78 | 16.37 | 33.94 |
| 1200 | 6.75 | 19.06 | 38.47 |
| 1500 | 7.53 | 21.35 | 42.99 |
| 1800 | 8.12 | 23.73 | 47.52 |
| 2400 | 9.49 | 25.96 | 53.4 |

**Table 7.** Speed of impregnation for sandblasted and polished concrete slabs and limestone.

| Substrate | Speed of impregnation ($\%/\sqrt{s}$) |
|---|---|
| Sandblasted concrete surface | 0.1935 |
| Polished concrete surface | 0.5518 |
| Limestone | 1.1218 |

**Fig. 8.** Evolution of porous volume versus pore diameter obtained by mercury porosimetry (Courard 1999).



second procedure produced different results from those obtained for the capillary absorption test (DIN 52617 1987). This can prevent absorption from lateral faces of the samples and consequently reduce the quantity of water absorbed.

Results obtained above confirm that a major part of the capillary action transfer happens within the first few seconds after the solid–liquid contact. After 20 s an important decrease in penetration rate is observed. To quantify this observation, one can calculate the absorption rate between 0 and 20 s

$$[6] \qquad v = \left(\frac{\Delta m_i}{\Delta m_o}\right)\sqrt{t}$$

where $v$ is the speed of impregnation ($\%/\sqrt{s}$), $\Delta m_i$ is the mass change at time $t_i$, $\Delta m_o$ is the mass change at time $t_o$ and $t$ is time. This coefficient (Table 7) depends on the nature of the liquid that has been absorbed as well as on its viscosity and surface free energy (eq. [4]). It gives a good representation of the transfer kinetics and water migration at the surface of the concrete substrate.

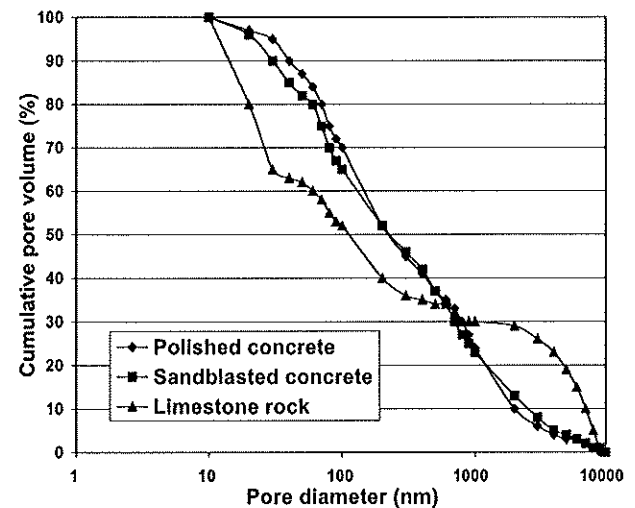### 4.3. Mercury intrusion porosimetry

As already mentioned, the present test is performed with the aim of observing some particular phenomena because of the shape of the pore entry. A complete pore distribution can be seen in Fig. 8 (Courard 1999), and the evaluation of the specific surface, the total porous volume, and the mean radius are given in Table 8.

Various observations can be made from mercury porosimetry.

- Pore volumes of sandblasted and polished concrete slab samples are the same. We must keep in mind that in this case mercury was able to intrude from all faces of the specimens because it was difficult to coat the unexposed faces. Results thus give a view of the real porous volume and its distribution on the first 5 mm of superficial concrete.
- The porous volume of limestone is about eight times less than that of concrete.
- Mean pore radius is the same for the two types of concrete samples and 10 times greater than that of limestone. This means that the heights observed in capillary suction are 10 times greater for limestone than for concrete (Jurin's law), while the rate of penetration ($l_p/\sqrt{t}$) for limestone is only one third that of the concrete. This value does not take into account the effect of the interfacial transition zone (Courard 1999).

However, it is already evident that the difference between sandblasted and polished concrete substrates is a question of capillary entry rather than internal porous structure. Moreover, it mainly concerns larger capillaries than those investigated by MIP.

### 4.4. Effect of cementitious products on capillary action

A last observation to be made is the replacement of water by cementitious solutions in absorption action tests. Table 9 shows the results of the capillary action test, first with pure water ($w$) and secondly with centrifuged solution ($c$) on the same specimen; the six specimens have been cored from the

Table 8. Results of mercury porosimetry on samples (5 mm × 5 mm × 5 mm) of sand-blasted (S) and polished (P) concrete slabs and limestone (R).

| Sample type | Specific surface ($m^2/g$) | Total porous volume ($cm^3/g$) | Mean pore radius (nm) |
|---|---|---|---|
| Sandblasted S1 | 1.68 | 0.0402 | 130 |
| Sandblasted S2 | 1.76 | 0.0472 | 193 |
| Sandblasted S3 | 1.98 | 0.0501 | 172 |
| Polished P | 1.87 | 0.0462 | 136 |
| Limestone R | 0.54 | 0.0058 | 12 |

same polished concrete slab. Statistical analysis based on the comparison of linear regression curves has been performed (95% confidence level).

Use of admixtures I, II, IV, and V seems to induce different behaviors versus pure distilled water absorption, but the differences between water absorption results are more significant. Results clearly demonstrate that unless water modifies the inner surface of pores or produces irreversible filling of them, it is more the specific pore structure rather than the thermodynamic or viscous properties of slurries that has any fundamental effect.

Moreover, we observe that the speed of penetration is sometimes high for both water and centrifuged solution. According to Washburn's law and considering a similar viscosity and mean pore radius, we have calculated the adhesion tension $\gamma_L \cos\theta$ (Courard 2002) of the different products (Table 10). The impregnation speed has been calculated between 0 and 60 s (Table 9), and the correlation with tension of adhesion (Fig. 9) was analyzed.

An increase in adhesion tension means a high value of $\gamma_L$ or a low value of contact angle $\theta$. According to Washburn's law, this will induce an increase in impregnation rate. This can explain the differences observed for capillary suction of centrifuged solutions, but not for those of water. Another factor that must be taken into account here is the internal skeleton of concrete by means of mean pore radius, which is another factor in Washburn's law.

## 5. Conclusions

The results of the different tests performed lead to the following conclusions.

* Adhesion cannot be explained solely on the basis of mechanical interlocking because of the roughness produced by surface preparation.
* The penetration of water or interstitial solutions of repair material into the concrete substrate is a fundamental parameter to be taken into account. According to Washburn's law, it depends on the thermodynamic properties of slurries and their viscosity as well as the pore radius of the substrate.
* Classical and standardized tests are not able to characterize the early behavior of the composite concrete substrate – repair material because the time interval defined for observations begins too late and is too large.
* The new capillary action test makes it possible to continuously record mass change of concrete samples and allows one to follow exactly what happens as of early contact

with the liquid phase and evolution over time of liquid capillary suction.

* Impregnation rate calculated between 0 and 20 s is an interesting discriminator parameter for the evaluation of transport kinetics and liquid migration at the interface.
* While mercury porosimetry analysis is a way to evaluate the shape of pores between 7.5 nm and 75 μm, the new capillary suction test exhibits a difference in behavior for large pores and capillaries.
* Washburn's law clearly defines the parameters influencing penetration rate: superficial tension and viscosity of liquid, contact angle of liquid on solid, and pore radius of the solid phase. These properties must be known exactly to promote penetration. One needs low values of contact angle, high values of superficial tension of liquid, and low viscosity of liquid. A higher mean pore radius will also allow a higher rate of liquid absorption, which means a higher probability of having contact sites and electrochemical interactions.
* Capillary entry shape has been shown to be an influencing parameter. This is related to the type of surface preparation that will induce a particular micro-shape of the extremity of the capillaries. Ink-bottle or circular shapes are commonly considered, but further information is needed.
* Absorption rates are greater for polished than for sandblasted concrete substrates. This means a fast wetting of the superficial layer of concrete and rapid penetration of water into the first millimetres of concrete. This will allow a better development of mechanical and chemical anchorage between the new material (slurries) and the substrate, because of a large interaction area.
* Analysis of water absorption does not give the same results as cementitious solutions absorption. The use of centrifuged part of cementitious pastes (eventually modified with admixtures) seems to be a good solution to approach real transport phenomena at the interface. Modification of surface free energy of liquid and contact angles can explain some different behaviors.

## Acknowledgments

**Table 9.** Capillary suction of water (w) and centrifuged (c) solutions on polished (P) concrete substrate (mass change in grams).

| Time (s) | Water P1w | Admixture I P1c | Water P2w | Admixture II P2c | Water P3w | Admixture III P3c | Water P4w | Admixture IV P4c | Water P5w | Admixture V P5c | Water P6w | Admixture VI P6c |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 0.09 | 0.28 | 0.11 | 0.22 | 0.14 | 0.18 | 0.24 | 0.31 | 0.07 | 0.39 | 0.3 | 0.3 |
| 10 | 0.12 | 0.4 | 0.16 | 0.32 | 0.2 | 0.22 | 0.33 | 0.36 | 0.12 | 0.47 | 0.35 | 0.4 |
| 15 | 0.13 | 0.47 | 0.18 | 0.38 | 0.23 | 0.24 | 0.44 | 0.4 | 0.15 | 0.53 | 0.4 | 0.45 |
| 20 | 0.14 | 0.51 | 0.2 | 0.42 | 0.26 | 0.26 | 0.5 | 0.43 | 0.18 | 0.58 | 0.45 | 0.48 |
| 25 | 0.15 | 0.55 | 0.2 | 0.46 | 0.28 | 0.28 | 0.54 | 0.44 | 0.21 | 0.61 | 0.49 | 0.51 |
| 30 | 0.16 | 0.57 | 0.22 | 0.49 | 0.3 | 0.29 | 0.58 | 0.47 | 0.23 | 0.64 | 0.51 | 0.53 |
| 35 | 0.17 | 0.6 | 0.24 | 0.52 | 0.31 | 0.31 | 0.66 | 0.48 | 0.25 | 0.67 | 0.54 | 0.55 |
| 40 | 0.17 | 0.62 | 0.25 | 0.54 | 0.33 | 0.32 | 0.71 | 0.48 | 0.27 | 0.69 | 0.57 | 0.56 |
| 45 | 0.18 | 0.64 | 0.25 | 0.56 | 0.35 | 0.34 | 0.74 | 0.49 | 0.28 | 0.71 | 0.59 | 0.58 |
| 50 | 0.19 | 0.66 | 0.27 | 0.59 | 0.36 | 0.36 | 0.76 | 0.51 | 0.3 | 0.74 | 0.62 | 0.59 |
| 55 | 0.2 | 0.68 | 0.28 | 0.6 | 0.37 | 0.38 | 0.78 | 0.52 | 0.32 | 0.77 | 0.64 | 0.6 |
| 60 | 0.2 | 0.69 | 0.29 | 0.63 | 0.38 | 0.38 | 0.81 | 0.52 | 0.33 | 0.77 | 0.67 | 0.61 |
| 300 | 0.49 | 1.15 | 0.6 | 1.2 | 0.73 | 0.78 | 1.77 | 0.74 | 0.79 | 1.42 | 1.41 | 1 |
| 600 | 0.77 | 1.64 | 0.88 | 1.75 | 1 | 1.15 | 2.57 | 0.93 | 1.13 | 1.88 | 2.05 | 1.4 |
| 900 | 0.99 | 2.02 | 1.09 | 2.19 | 1.22 | 1.49 | 3.17 | 1.11 | 1.41 | 2.31 | 2.55 | 1.76 |
| 1200 | 1.19 | 2.35 | 1.29 | 2.58 | 1.41 | 1.79 | 3.68 | 1.26 | 1.65 | 2.7 | 2.98 | 2.09 |
| 1500 | 1.36 | 2.68 | 1.46 | 2.95 | 1.57 | 2.05 | 4.09 | 1.37 | 1.87 | 3.06 | 3.36 | 2.39 |
| 1800 | 1.53 | 2.95 | 1.61 | 3.24 | 1.72 | 2.3 | 4.45 | 1.53 | | | | |

**Table 10.** Tension of adhesion and speed of impregnation of water (w) and centrifuged cement slurries (c) on polished (P) concrete surfaces.

| Sample reference | Tension of adhesion (mN/m) | Speed of impregnation ($\%/\sqrt{s}$) |
|---|---|---|
| P1w | 38.2 | 0.1572 |
| P1c | 65.5 | 0.559 |
| P2w | 38.2 | 0.2172 |
| P2c | 68.2 | 0.4861 |
| P3w | 38.2 | 0.2627 |
| P3c | 64.9 | 0.2792 |
| P4w | 38.2 | 0.6157 |
| P4c | 46.7 | 0.3318 |
| P5w | 38.2 | 0.2537 |
| P5c | 59.5 | 0.5119 |
| P6w | 38.2 | 0.5094 |
| P6c | 62 | 0.4566 |

**Fig. 9.** Analysis of the correlation between the speed of impregnation and thermodynamic properties of modified cement slurries.

$$y = 17.849 \mathrm{Ln}(x) + 76.087$$
$$R^2 = 0.5798$$
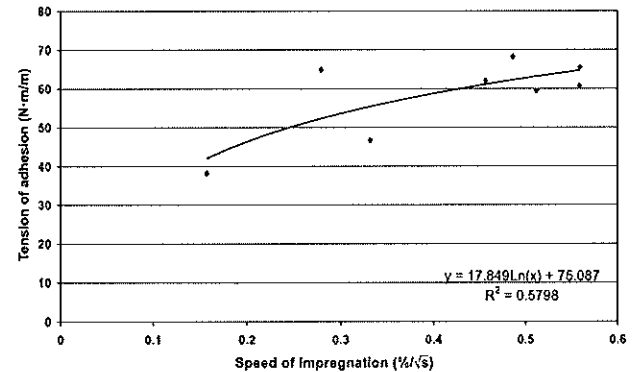
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## List of symbols

$g$  gravitational acceleration

$H$  height of liquid penetration

$l_p$  penetration length

$p$  capillary pressure

$p_a$  atmospheric pressure

$p_w$  water pressure

$r$  pore radius

$t$  time

$\gamma_c$  critical surface tension of wetting

$\gamma_L$  surface free energy of liquid

$\eta$  viscosity of liquid

$\theta$  contact angle