

# Efficiency and durability of surface protection products of concrete

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## Abstract

*Steel corrosion induced by the penetration of aggressive agents (chlorides, carbon dioxide ...) from the environment is the main pathology that questions the durability of reinforced concrete structures. In order to prevent and/or limit the risk of corrosion by carbonation of some concrete structures, it is envisaged to use surface protection products to limit the exchange mechanisms between concrete and the environment. The protection products will act only by clogging the surface pores and/or micro-cracks of the concretes, thus preventing the penetration and the diffusion of external agents such as CO<sub>2</sub> and O<sub>2</sub> from the atmosphere into the cement matrix. The standard NF EN 1504-2 classifies these protection products in three families:*

- Coating products that produce a continuous protective layer on the surface that acts as a physical barrier against the penetration of aggressive agents (i.e. epoxy, acrylic and polyurethane resins).*
- Impregnation products that reduce porosity of the concrete skin. These products can be of two different natures, organic (epoxy, acrylic ...) or inorganic (sodium silicate, nano silica...).*
- Hydrophobic impregnation products that create a water repellent surface; the pores are not filled but their inner surface is coated.*

*As part of this study one product from each family was selected: acrylic impregnation product, acrylic coating and silanes / siloxanes-based product (hydrophobic impregnation). This work has the objective to evaluate the efficiency and the durability of the selected surface protection products by investigating their impacts on concrete carbonation and transport properties (gas diffusion). With that in mind, different experimental devices (carbonation chamber, diffusion cells) are used.*

## Keywords: durability; concrete; coating; impregnation; transport properties

### 1. Introduction

The corrosion of the reinforcement is one of the most serious pathologies affecting reinforced concrete structures. It occurs when aggressive agents such as carbon dioxide penetrate and diffuse into the cement matrix until they reach the reinforcements. In this case we talk about carbonation-induced corrosion.

The steel of reinforced concrete is a thermodynamically unstable material that tends to converge towards a more stable state (oxide). In a basic environment such as concrete (pH = 13), this steel forms a passivating layer on its surface which protect it from corrosion as shown in (Figure 1). The drop in pH (from 13 to 8.5) caused by carbonation causes the depassivation of the reinforcement which in the presence of water and oxygen begins to corrode.

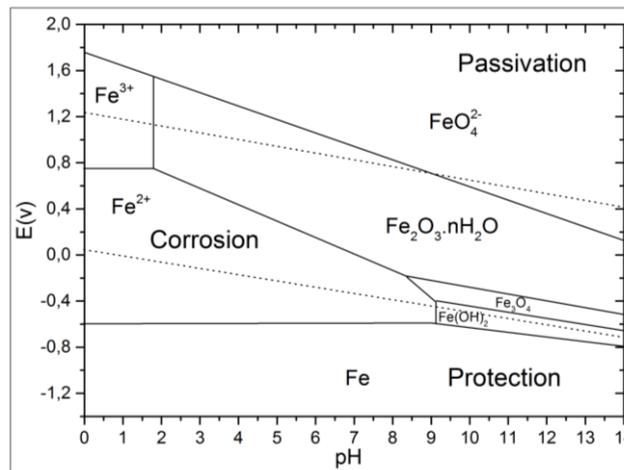
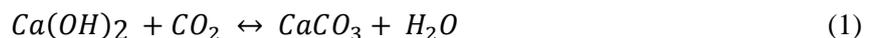
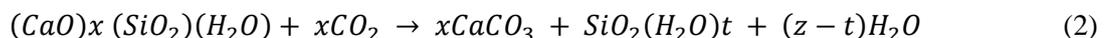


Figure 1: Pourbaix diagram for Fe/H<sub>2</sub>O system at 25 °C (SHE)

The carbonation phenomenon occurs when carbon dioxide is present in the diffuse atmosphere in gaseous form in the cement-based material through cracks and superficial pores. Once inside, it can react with the hydrates of the cement. Carbonation leads to the consumption of alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and calcium hydroxides (portlandite) and therefore to the loss of the buffer effect. The kinetics of carbonation is at its maximum when the relative humidity (RH) is around 50-70% [1]. This carbonation occurs at different steps: CO<sub>2</sub> dissolves in the interstitial solution to give carbonate ions, then carbonic acid (H<sub>2</sub>CO<sub>3</sub>) dissolves in water in two phases (HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>), the speciation is based on the pH. The acidification of the interstitial solution caused by the dissolution of CO<sub>2</sub> in the interstitial solution leads to dissolution of the hydrates, in particular portlandite Ca(OH)<sub>2</sub> which partially dissolves to restore the basicity of the environment according to the following reaction:



C-S-H also carbonate, resulting in the consumption of calcium ions in the gel and leading to the formation of an amorphous silica [2]:



The kinetic of carbonation depends on the diffusion of CO<sub>2</sub> in cementitious materials. Therefore, gaseous diffusion will be approached in the second part of this study.

Diffusion is a natural shift of chemical species from regions of higher concentrations to those of lower concentrations. Fick's laws describe this phenomenon:

$$J = -D \frac{\partial c}{\partial x} \quad (3)$$

Where J is the mass transport rate (mol /m<sup>2</sup>.s), D the diffusion coefficient (m<sup>2</sup>/s),  $\frac{\partial c}{\partial x}$  is the concentration gradient (mol/m<sup>4</sup>), and x is the thickness of the material (m).

In order to limit the diffusion of carbon dioxide and therefore the carbonation of concrete, it is possible to apply protection products described by the standard EN NF 1504-2 [3]. These products are classified into three families:

- Coating
- Impregnation
- Hydrophobic impregnation

As part of this study one product per family will be studied (Table 2)

Coating products produce a continuous protective layer on the surface that acts as a physical barrier against the penetration of aggressive agents (i.e. epoxy, acrylic and polyurethane resins). Li et al [4] compared the effectiveness of some organic coatings against carbonation and show that the coating products tested allow the reduction of the carbonation depth compared to untreated samples.

Impregnation products reduce porosity of the concrete skin. These products can be of two different natures, organic (epoxy, acrylic ...) or inorganic (sodium silicate, nano silica...). Many research works [5][6][7][8], have been done to evaluate the effectiveness of silica-based impregnation products and have shown that some products such as sodium silicate and ethyl silicate are effective against carbonation.

The last family is hydrophobic impregnation products. These products create a water repellent surface, the pores are not filled but their inner surface is coated. The organic compounds used as water-repellent agents are most often silanes and siloxanes. The latter condenses to form polysiloxanes (silicon resin) which bind strongly to the surface of the hydration products by means of covalent siloxane bonds. Zhang et al [9] compared the effectiveness of different hydrophobic protection products against carbonation and have shown that silane-based products greatly reduce the carbonation depth.

The contribution of this study is to compare the effectiveness of these three families of products against carbonation and gaseous diffusion on uncracked materials but also on cracked materials. The test campaign and the results will be presented and discussed in the following parts.

## 2. Materials and methods

### 2.1 Materials and specimen preparation

In this study, standard CEM I mortar samples of different sizes and geometries were made. The composition is described in the Table 1. The samples are demolded after 24 hours and are then cured for at least 28 days in water (with lime). In order to evaluate the protective effect of surface protection products against carbonation at the steel / mortar interface, centimetric prisms (7×7×28 cm) with a 6 mm diameter steel bar in the middle were manufactured (Figure 2). These specimens are intended for the study of carbonation on cracked materials.

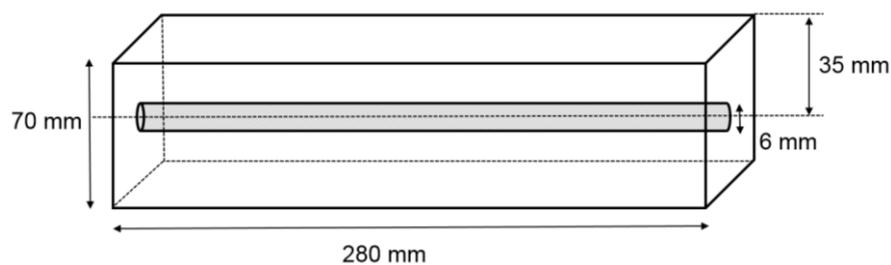


Figure 2: Schematic representation of the prismatic specimen

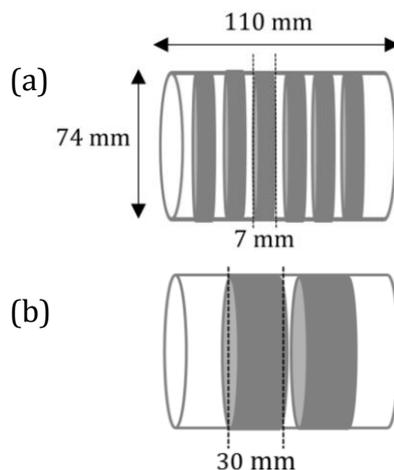


Figure 3 : Schematic representation of the cylindrical specimen for: (a) diffusion test; (b) carbonation

Cylindrical samples of mortar (110 mm × 74 mm) are also made. 7 mm thick discs are obtained after cutting these samples (Figure 3 (a)) and they are intended for diffusion tests and 30 mm thick discs (Figure 3 (b)) are used for the study of carbonation on uncracked material. The surface protection products used in this study are described in the Table 2.

Table 1 : Formulations of cementitious materials

Compound	Characteristics	Quantity (kg/m <sup>3</sup> )
Cement	CEM I 52.5	514
Sand 0/4 mm	Siliceous (EN 196-1)	1543
Water		257

Table 2 : The different products studied

Ref	Nature of product	Type	Number of layers
Ref	Untreated sample	-	-
AI	Acrylic impregnation	Impregnation	3
SC	Silane based cream	Hydrophobic impregnation	3
AC	Acrylic coating	Coating	2

### 2.3 Cracking of the prismatic specimens

After 28 days of cure, the prisms are pre-cracked using three-point bending test as shown in figure 4. The intended residual openings are: 100 and 500  $\mu\text{m}$ . The control of these openings is done via a displacement sensor, Linear Variable Differential Transformer (LVDT) which is linked to software that also controls the load (value of the load, loading rate). Figure 5 shows the loading values required to obtain desired residual opening cracks and the corresponding under loaded crack openings.

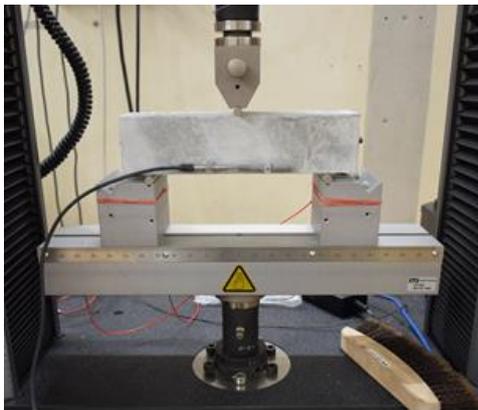


Figure 4 : Three-point bending test on  $70 \times 70 \times 280$  mm specimens

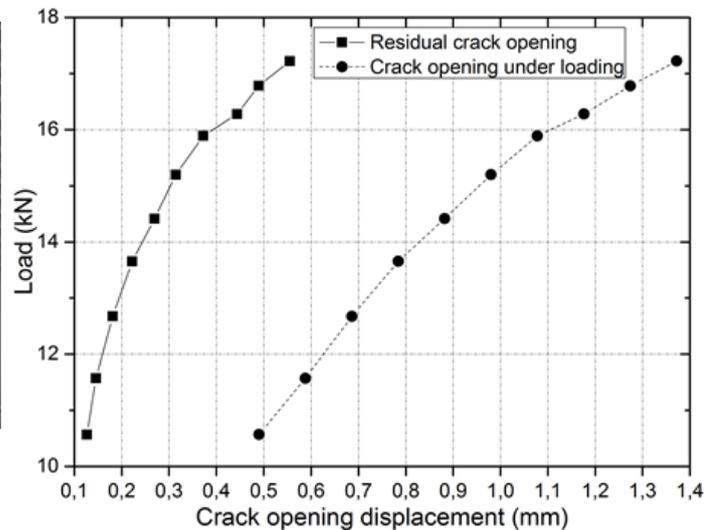


Figure 5: Range of residual crack openings obtained by the three-point bending test

### 2.4 Accelerated carbonation

The uncracked samples were wrapped with an adhesive aluminum tape leaving only one face exposed to carbonation they were then pre-conditioned at (25 °C, 55 % RH) for 7 days before the products were applied. They were put into accelerated carbonation (3% CO<sub>2</sub>, RH = 55%, 25 °C) 7 days later. The period of this accelerated carbonation is between 14 days and up to 90 days.

The accelerated carbonation device used for this study was described by Ghantous et al [10].

The cracked samples were pre-conditioned at (25 °C, 55 % RH) for 1 month before the application of the products. The products are applied over the entire perimeter of the prism, over a width of  $3 \pm 1$  cm on either side of the crack as shown in figure 6. They were put into accelerated carbonation (3% CO<sub>2</sub>, RH = 55%, 25 °C) for 7 days later.

The carbonation depth is determined after splitting the sample and application of the phenolphthalein which allows to identify the change in pH of the interstitial solution. The non-carbonated part (pH > 9-10) is colored pink while the carbonated part (pH < 9-10) does not change color.

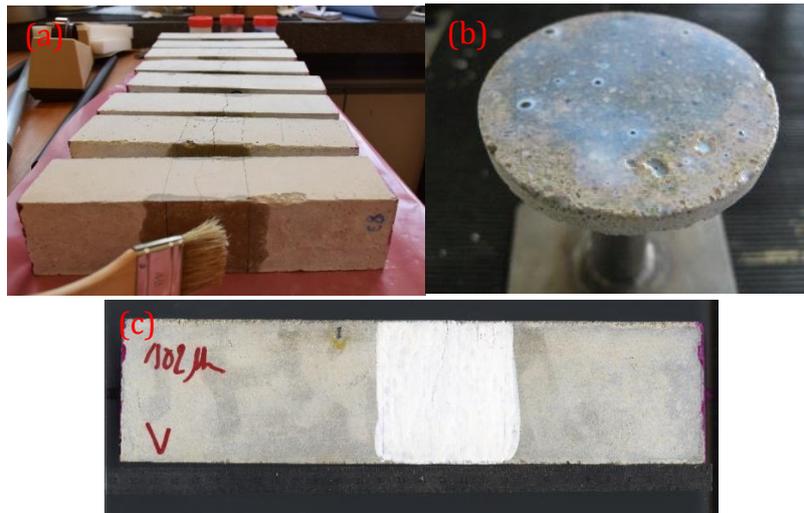


Figure 6 : Photos of samples during and after application of the products: (a) application of SC on prismatic (cracked) samples; (b) application of AI on cylindrical (uncracked) samples; (c) prismatic sample after application of AC.

The carbonation length along the crack path and along the load-induced damage of steel/mortar interface is obtained in the same way (Figure 7)



Figure 7 : (a) Carbonation length of the steel/mortar interface for cracked carbonated specimen; (b) Carbonation depth of uncracked specimen

## 2.5 Gas diffusion

After cutting the discs intended for the diffusion test, they were placed in a drying cabinet until the hydric balance was reached. The diffusion test was then carried out on the samples before and 7 days after application of the products.

The principle of the gaseous diffusion test is to place the sample (cementitious material) between two perfectly sealed compartments, upstream and downstream respectively containing air (80% N<sub>2</sub> and 20% O<sub>2</sub>) and pure nitrogen. The goal is to generate a concentration gradient between the two surfaces of the sample to create a gaseous diffusion flux (Figure 8).

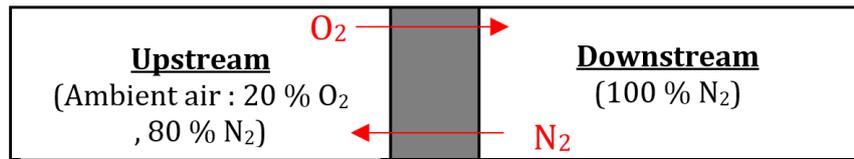


Figure 8 : Principle of the gaseous diffusion test

To carry out this test, stainless steel diffusion cells are used. They are equipped with oxygen and pressure sensors and thermocouples connected to a computer with recording software.

The gases that make up the gaseous phase (nitrogen and oxygen) are supposed to be perfect. They therefore obey the law of perfect gases. They can dissolve in the liquid phase according to Henry's equilibrium, so it is possible to connect their concentrations at their partial pressures. The mass conservation equations of the mobile constituents of the porous medium form the basis of modeling.

The degree of saturation of the material remains constant during the test. Therefore, liquid phase transport can be neglected. During the gas diffusion test, the pressure of the gas mixture remains constant. The phenomenon of convection can thus be neglected, the equation of conservation of the mass of a gas  $j$  can therefore be written as follows:

$$\frac{\partial P_{gj}}{\partial t} = \frac{D_e^j}{\phi(1-S_l)} \frac{\partial^2 P_{gj}}{\partial x^2} \quad (4)$$

Or

$$\frac{\partial X_j}{\partial t} = \frac{D_e^j}{\phi(1-S_l)} \frac{\partial^2 X_j}{\partial x^2} \quad (5)$$

With 
$$X_j = 100 \times \frac{P_{gj}}{P_g} (\%) \quad (6)$$

With:  $D_e^j$  the effective diffusion coefficient in the gas mixture;  $P_{gj}$  the partial pressure of the gas  $j$ ;  $\phi$  the porosity;  $S_l$  the liquid water saturation;  $\rho_i$  density;  $X_j$  the concentration of gas  $j$  in the gas mixture.

The MIED tool (Diffusion Experiment Interpretation Model), developed at the CEA, calculates the analytical solution of the diffusion equation. It is a dynamic library (coded in Fortran 90 and Visual Basic), coupled with the Excel solver allowing the calculation of instantaneous concentrations upstream and downstream based on the analytical diffusion equations.

## 3 Results

### 3.1 Carbonation of uncracked specimen

The results of this study (Figure 9) show that all the products are effective against carbonation. By looking in more detail, the carbonated depth of the AI and SC treated samples is about 5.5 mm after 90 days while that of untreated sample which is approximately 8 mm for the same period.

This reduction in carbonation depth provided by the silane cream (SC) is consistent with the results of the study of Zhang et al [9]. This product slows down the carbonation phenomenon because it dries the sample. The lack of water greatly reduces the dissolution of  $\text{CO}_2$  and therefore the formation of carbonic acid. The reduction of carbonation carried by acrylic impregnation is probably due to the clogging effect of the surface pores.

Concerning AC, this product considerably reduces the carbonation kinetics. Indeed, the carbonated depth of AC treated samples is 3.2 mm after 90 days of exposure. This acrylic coating forms a continuous film on the surface of samples, considerably reducing CO<sub>2</sub> penetration.

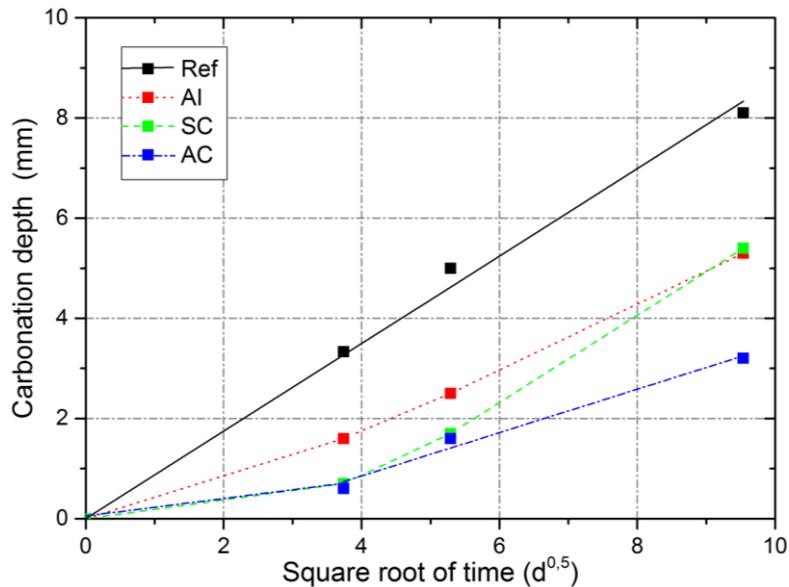


Figure 9: Carbonation depth with respect to square root of time

It is therefore necessary to pay attention to the kinetics of carbonation for treated samples which do not follow the classical law in square root of time, showing that carbonation retrained could be limited to a short term.

### 3.2 Carbonation of cracked specimen

The results (Figure 10) show that SC is not effective against carbonation on cracked materials, even for crack openings of 100  $\mu\text{m}$ . Indeed, this product does not have the ability to seal cracks with this opening. Concerning the other products, AI and AC seem to be able to fill the opening cracks between 100  $\mu\text{m}$  and 500  $\mu\text{m}$  because the carbonated length in the steel/mortar interface is greatly reduced by the application of these two products. Indeed, for a crack opening of 100  $\mu\text{m}$ , the carbonated length in the prisms treated with these two products is less than 1 cm at 90 days while that measured in untreated prisms is about 6.5 cm. The same trend is observed for a crack opening of 500  $\mu\text{m}$ , the carbonated length in prisms treated with AI and AC is about 2 cm at 90 days while that measured in untreated prisms is about 9 cm.

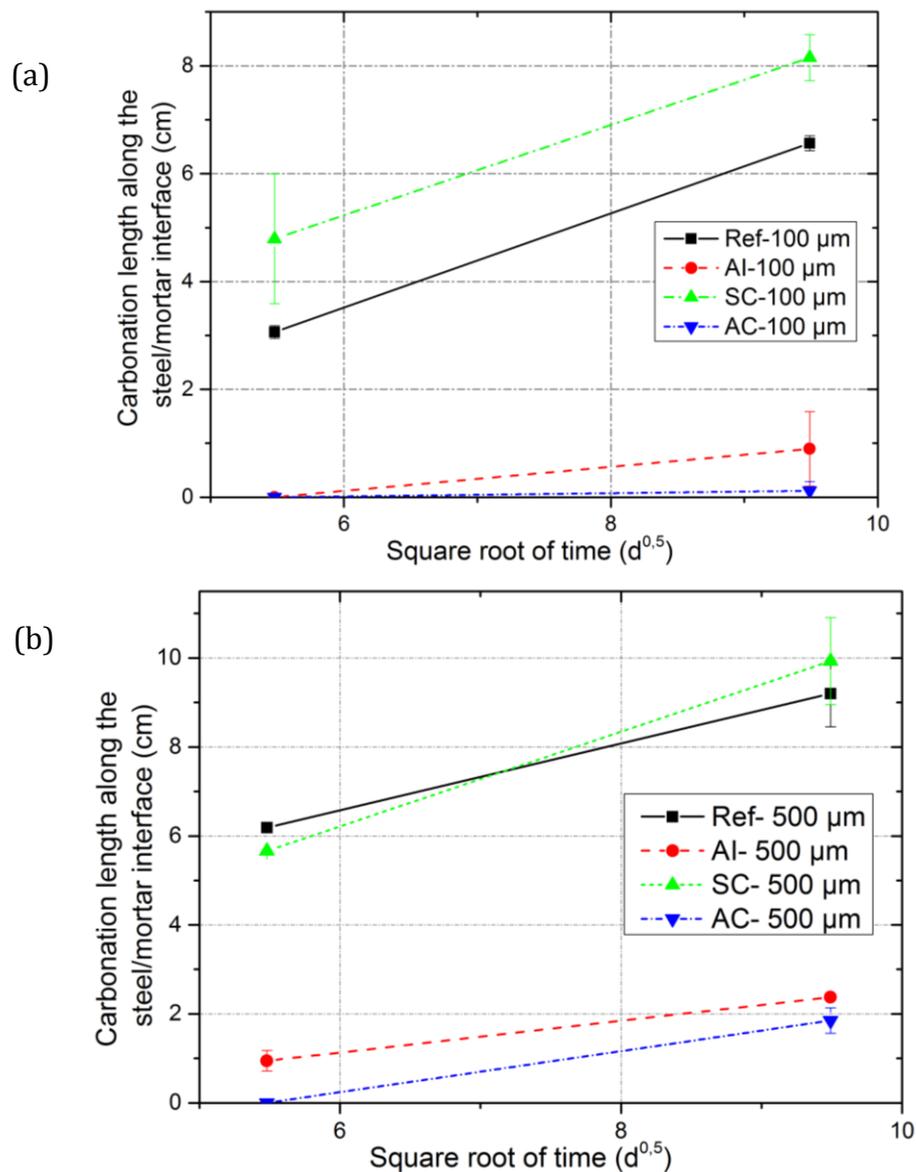


Figure 10: Carbonation length along the steel/mortar interface with respect to square root of time: (a) 100  $\mu\text{m}$  crack opening; (b) 500  $\mu\text{m}$  crack opening

Again, a longer experiment would be useful to characterize the aging of treatments in case of cracked samples.

### 3.1 Gas diffusion

The results presented in (Table 3) and (Figure 11) show the effectiveness of all the products tested. This efficiency is characterized by the ratio (diffusion coefficient of the material before treatment / after treatment). The gain obtained differs from one product to another and this difference can reach an order of magnitude. Indeed, AC can achieve a gain of about 14. As for the other two products, the AI and SC, they bring a gain between 3.9 and 4.8. The maximum effectiveness of AC can be explained by the fact that this product forms a continuous coating film on the surface of mortar, which slows the penetration of external agents such as  $\text{O}_2$  or the  $\text{N}_2$ . This is not the case for the other products which are impregnation products which thus penetrate the cement matrix to reduce the surface porosity.

Table 3: Results of diffusion tests

Product	Sample	Diffusion coefficient before treatment (m <sup>2</sup> /s) (D <sub>1</sub> )		Diffusion coefficient after treatment (m <sup>2</sup> /s) (D <sub>2</sub> )		Gain = D <sub>1</sub> /D <sub>2</sub>	
		Upstream (D <sub>N2</sub> )	Downstream (D <sub>O2</sub> )	Upstream (D <sub>N2</sub> )	Downstream (D <sub>O2</sub> )	Up-stream	Down-stream
AC	S1	8.6 10 <sup>-8</sup>	7.6 10 <sup>-8</sup>	5.4 10 <sup>-9</sup>	5.4 10 <sup>-9</sup>	15.9	14.1
	S2	8.8 10 <sup>-8</sup>	8.3 10 <sup>-8</sup>	6.7 10 <sup>-9</sup>	6.4 10 <sup>-9</sup>	13.1	13.0
SC	S1	5.4 10 <sup>-8</sup>	5.4 10 <sup>-8</sup>	1.4 10 <sup>-8</sup>	1.3 10 <sup>-8</sup>	3.9	4.2
	S2	5.2 10 <sup>-8</sup>	5.0 10 <sup>-8</sup>	1.3 10 <sup>-8</sup>	1.2 10 <sup>-8</sup>	4.0	4.2
AI	S1	6.2 10 <sup>-8</sup>	5.8 10 <sup>-8</sup>	1.3 10 <sup>-8</sup>	1.3 10 <sup>-8</sup>	4.8	4.5
	S2	7.5 10 <sup>-8</sup>	6.3 10 <sup>-8</sup>	1.6 10 <sup>-8</sup>	1.5 10 <sup>-8</sup>	4.7	4.2

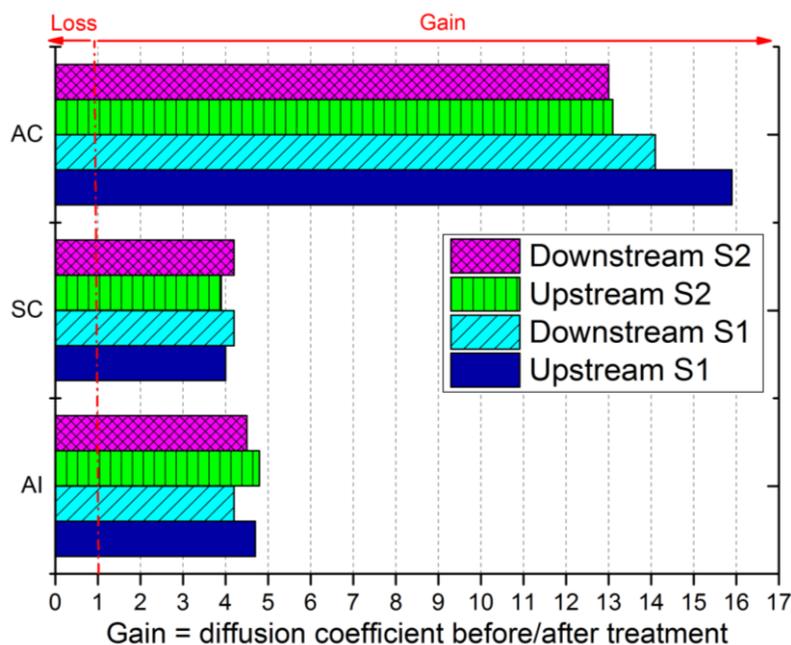


Figure 11 : Histogram of the gains brought by the different products with respect to gaseous diffusion

## 4 Conclusion

- (1) The results of this study show that the products studied, belonging to three families of protective products (impregnation, impregnation and coating), bring an important contribution in protecting the surfaces of cementitious materials against the penetration and diffusion of aggressive external agents such as CO<sub>2</sub> and O<sub>2</sub>. The results of the gaseous diffusion study show this. Indeed, reductions by a factor of 4 to 15 were observed.
- (2) The reduction of gaseous diffusion through the samples provided by the protection products leads to the reduction of the carbonation kinetics. Indeed, the carbonation depth are reduced by about half when applying the products.
- (3) For cracked samples, the carbonated length at the steel/mortar interface is significantly reduced by AC and AI. These two products appear to have both a protective power on uncracked materials and are also capable of sealing cracks of a few hundred μm. This is not the case with SC, which does not seem to be able to seal cracks.

- (4) These results show that the products tested are effective in the short term. Accelerated aging tests (hydrous cycles, UV lamps) are underway to evaluate the long-term effectiveness of these products.

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