



Performance of Protected Concrete against Chemically Aggressive Environments

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ABSTRACT

Three different types of surface protections were tested: silicone hydrophobic agent, acrylic and epoxy coatings. Surface treatments act as a barrier between the environment and the concrete, preventing or retarding the entry of harmful substances and cutting off the transportation path into concrete. There is a linear relation between the ionic permeability of the resin and the electrolytic conductivity of the resin. Virtually all the surface protections are permeable to water, enough to be little effective controlling the corrosion but not the ionic permeability which is much lower. It seems to be a connection between the permeability and the characteristics of the density of the crosslinking of the coating. The water (or aggressive solution) is transported through the film in a process with several phases called permeation, which depends on two independent parameters: the solubility of the water in the polymer and its diffusivity or ability to pass through the film, both concerning the molecular structure of the resin. The effectiveness of a surface protection preventing the permeation depends on how close and strongly connected are the resin molecules. This work intends to contribute to a better understanding of the performance of protected concrete in chemically aggressive environments, by presenting results of ion diffusion and resistance to aggressive solutions of several hydrophobic agents and coatings used to protect concrete. The results indicate that the overall performance of epoxy resin was better than that of other types of protections.

KEYWORDS: silicone hydrophobic agent, acrylic coating, epoxy coating, protected concrete

1 INTRODUCTION

Concrete can be a highly durable construction material as long as care and quality control are enforced at all stages of the design, production and construction processes. However, experience has demonstrated that its potential long-term durability is not always achieved; leading to early failure of reinforced concrete structures [1]. It should be recognized that concrete is intrinsically a porous material, despite the improvements on its formulation and quality control to the best possible extent, it is not possible to prevent completely the ingress of potentially harmful agents. Micro-cracks and macro-pores will always exist on the concrete surface, providing a path for the transportation of aggressive ions into the interior of concrete [2].

It is now accepted that the durability of the reinforced concrete depends mainly on the composition and properties of the concrete surface layer [3]. This layer, sometimes with a thickness close to the cover of the

reinforcement, is most of the times the only responsible for the corrosion protection of the reinforcement. Surface treatments act as a barrier between the environment and the concrete. They prevent or retard the entry of harmful substances such as water, chlorides, etc. [4]. Surface coatings with appropriate "barrier" characteristics can cut off the transportation path into concrete. The standard EN 1504-2 [5] establishes as a minimum requirement for the coated concrete ingress that the capillary absorption and the water permeability coefficient should not exceed $0.1 \text{ kgm}^{-2}\text{h}^{-0.5}$ and the CO_2 permeability should at least correspond to a S_D value of 50 m.

Swamy and Tanikawa [6] evaluated the effect of concrete coatings to preserve concrete durability and concluded that the application of an impervious surface coating to concrete is a very attractive solution to protect new and existing concrete structures. However, with a wide range of coatings available in the market, it becomes extremely difficult to choose the right type of hydrophobic agent or coating, since similar generic types are known to possess considerably different diffusion characteristics [7]. The performance of the available generic types under different service conditions needs to be studied. There is also a need to develop performance criteria for evaluation of concrete protection materials and guidelines for the selection of hydrophobic agents and coatings appropriate for various exposure conditions [8].

2 EXPERIMENTAL PROGRAM

2.1 Materials

To evaluate the influence of cement, two types were used: a Portland cement (CEM I 42.5R) and a pozzolanic one (CEM IV/A (V) 32.5R), made with 35% of fly ash, according to EN 197-1 [9]. Table 1 shows the oxide composition of the cements. Table 2 presents the estimated compound composition of the cements using Bogue's expressions. Crushed granite with a density of 2566 kg/m^3 , water absorption of 2.1%, fineness modulus of 5.89 and a maximum size of 9.53 mm was used as a coarse aggregate, while crushed sand with a density of 2477 kg/m^3 , water absorption of 1.36 %, fineness modulus of 3.16 and a maximum size of 4.76 mm was used as a fine aggregate in the preparation of concrete specimens.

Table 1. Oxide composition of the cements

Chemical composition	CEM I 42.5R (%)	CEM IV/A (V) 32.5R (%)
SiO_2	19.64	39.24
Al_2O_3	4.34	4.80
Fe_2O_3	3.10	3.57
CaO	62.82	43.67
MgO	2.43	1.81
SO_3	3.33	2.81
Cl ⁻	0.02	0.02
Loss on ignition	3.2	2.80
Insoluble residue	0.90	26.10

Three types of concretes were used. The composition of the concretes is presented in Table 3. The concretes I-A and IV had a water-cement ratio of 0.60 and a cement content of 320 kg/m^3 . The concrete I-B was made with CEM I, a water-cement ratio of 0.40 and a cement content of 500 kg/m^3 . The slump test achieved values of about 60 mm for concretes I-A and IV. The concrete I-B presented a slump of 180 mm. The average compressive strength of the concrete I-A attained 27.5 MPa at 28 days of age, the concrete I-B 55.6 MPa and the concrete IV 20.8 MPa. The experimental campaign was designed in order to test concrete specimens without any type of hydrophobic agent or coating and treated concrete specimens.

Table 2. Estimated compound composition of the cements

Compound composition	CEM I 42.5R (%)	CEM IV/A (V) 32.5R (%)
C ₃ S	64.39	27.70
C ₂ S	5.24	16.83
C ₃ A	6.26	6.69
C ₄ AF	9.42	10.85

Table 3. Composition of the concretes

Materials	Quantities (kg/m ³)		
	Concrete I-A	Concrete I-B	Concrete IV
Cement CEM I	320	500	-
Cement CEM IV	-	-	320
Gravel 5 – 10	796	888	814
Sand 0 – 5	940	690	898
Water	181	184	180
Superplasticizer	-	5	-

Concrete hydrophobic agents and coatings were selected to represent the following three generic types:

- i. Silicone agents (S);
- ii. Acrylic coatings (A);
- iii. Epoxy coatings (E).

Each generic type was represented by two products from different suppliers. The selection was made as presented in a previous paper [10]. Table 4 shows the properties of the selected concrete hydrophobic agent and coatings. All the products were applied on the substrate by brush following the recommendations of the suppliers and after drying of the specimens under laboratory conditions for at least 7 days.

Table 4. Description of the selected hydrophobic agent and coatings

Generic type	Silicone	Acrylic	Epoxy
	siloxane resin in solvent base	acrylic resin aqueous based	two component epoxy resin
Consistency	liquid	dense liquid	dense liquid
Coverage rate (m ² /dm ³)	2.8	3.5	4.0
Density at 20 °C (kg/dm ³)	0.83	1.40	1.30
Brookfield viscosity at 20 °C (mPa.s)	11	6000	1500
Surface drying time (min)	60	40	300
Interval between coats (h)	2	24	24

2.2 Penetration of chlorides

The characterization of the resistance to chlorides penetration was made with tests based on a non-steady state, procedure known as CTH Rapid Method developed by Luping [11]. The depth of penetration of the chloride front is determined by a colorimetric method using silver nitrate. The average penetration, measured with a precision of 0.5 mm, was considered to be the depth of penetration. The diffusion coefficient is obtained using the equation:

$$D = \frac{R \cdot T \cdot L}{z \cdot F \cdot U} \cdot \frac{x_d - \alpha \cdot \sqrt{x_d}}{t} \quad (1)$$

with:

$$\alpha = 2 \cdot \sqrt{\frac{R \cdot T \cdot L}{z \cdot F \cdot U}} \cdot \operatorname{erf}^{-1} \left(1 - \frac{2 \cdot c_d}{c_0} \right), \quad (2)$$

where D: diffusion coefficient, m²/s; z: absolute value for ion valence, for chlorides, z = 1; F: Faraday constant, F = 9.648 x 10⁴ J/(V.mol); U: absolute value of potential difference, V; R: gas constant, R = 8.314 J/(K.mol); T: solution temperature, K; L: specimen thickness, m; x_d: penetration depth, m; t: test duration, seconds, t = t_{CTH} x 3600; erf⁻¹: inverse of error function; c_d: chloride concentration at which the colour changes, c_d ≈ 0.07 N; c₀: chloride concentration in the upstream cell, N.

After the production of the concretes, cylinders with Ø110x230 mm were moulded. These cylinders were cut in cylinders with Ø110x50 mm, in order to obtain the specimens used in the tests. The hydrophobic agent and the coatings were applied when the concrete had 28 days. Before applying these products the concrete specimens stayed 7 days outside water, in order to guarantee that the surfaces are not in wet conditions. The products were only applied in one face of the cylinders. The instructions of the supplier of the products were followed during all the process. The tests occurred 7 days after hydrophobic agent or coatings were applied on concrete specimens. Figure 1 shows one test in development.

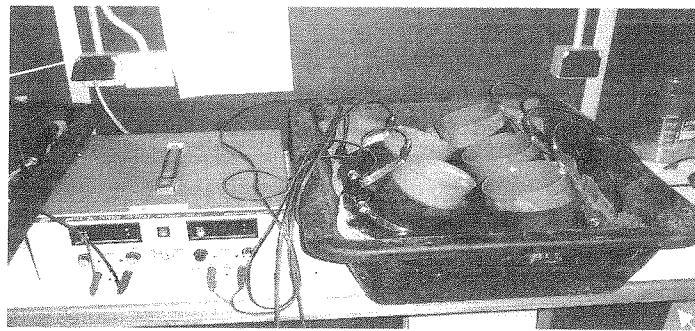


Figure 1. Test of penetration of chlorides.

After the time needed for the conclusion of the test, the specimens were taken-out from the equipment and broken in two halves by the mean of diametric compressive test. The solution of silver nitrate was then applied on the concrete surface and the colorimetric test was made in order to measure the depth of chlorides penetration (Figure 2). Five specimens of each product and composition were tested.

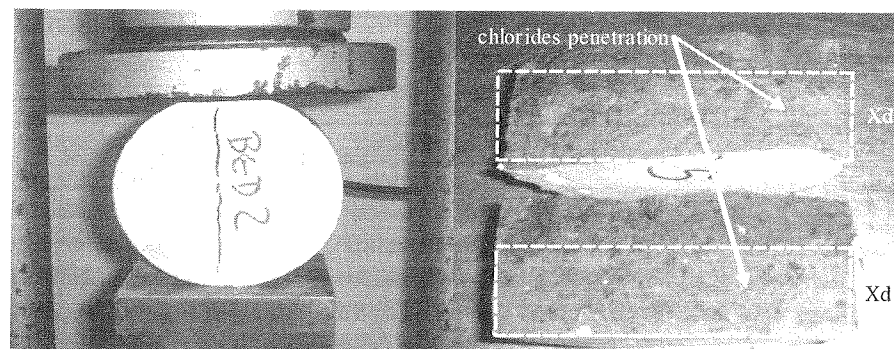


Figure 2. Colorimetric test of one specimen.

Table 5 and Figure 3 present the results of penetration of chlorides in a non-steady regime. In the case of the epoxy resin the diffusion coefficient was null. For concretes with similar composition, the penetration of chlorides depends on the porosity of the surface. Higher is the porosity less will the current that pass through the concrete surface. The porosity depends on the solids volume, on the thickness and type of the protection used. Epoxy resins with a solvent base have good resistance to chlorides penetration because they become strong and with low porosity [12].

Table 5. Diffusion coefficients for different types of paintings and concretes

References	Cement	Coating	C (kg/m ³)	a/c	D (10 ⁻¹² m/s)
Concrete I-A	CEM I	uncoated	320	0.60	14.40
Concrete I-B	CEM I	uncoated	500	0.40	6.90
Concrete IV	CEM IV	uncoated	320	0.60	9.87
Concrete SIL I-A	CEM I	silicone	320	0.60	4.68
Concrete SIL I-B	CEM I	silicone	500	0.40	2.04
Concrete ACR I-A	CEM I	acrylic	320	0.60	6.53
Concrete ACR I-B	CEM I	acrylic	500	0.40	3.86
Concrete EP I-A	CEM I	epoxy	320	0.60	0.00
Concrete EP I-B	CEM I	epoxy	500	0.40	0.00

The concrete hydrophobic agent and coatings decreases significantly the diffusion coefficient of the tested concretes. All unprotected concretes presented higher diffusion coefficients than the protected concretes. The concrete I-B, with high cement content and a low water-cement ratio, presented without any protection a good resistance to chlorides penetration. The concrete ACR I-A presented only a diffusion coefficient 5.4 % lower than the concrete I-B, with a comparable performance.

The silicone agent presented the best performance after the epoxy resin. The silicone has a reaction with the cement matrix that forms a hydrophobic layer at the pores walls. This protects the concrete from the ingress of the chlorides. The concrete IV presented a diffusion coefficient 31.5 % lower than the diffusion coefficient of concrete I-A, with the same water-cement ratio and the same cement content 320 kg/m³. This can only be explaining by the additions of the cement IV that ameliorate the behaviour of the concrete in presence of chlorides.

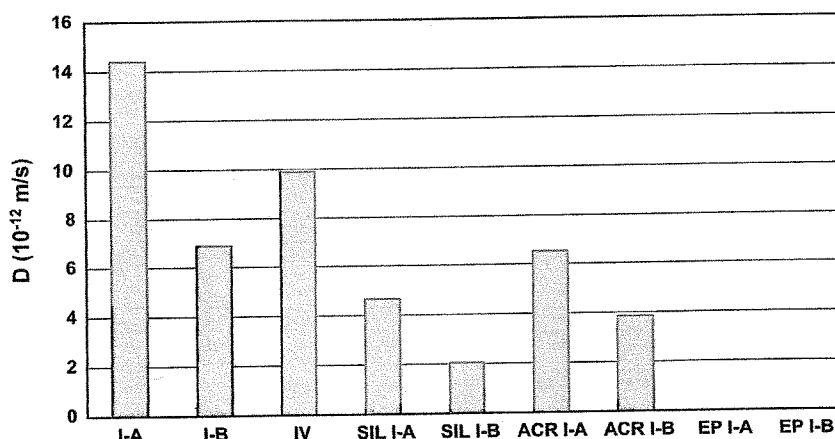


Figure 3. Coefficients of diffusion in a non-steady regime for different concretes, hydrophobic agent and coatings.

2.3 Sulphate attack

The sulphates can appear in the concrete by two origins: inside or outside sources [13]. The Portland cement has calcium sulphate as constituent. The water present in concrete could also have sulphates. Regarding outside sources of sulphates, there are many possibilities: atmospheric pollution, soils, industrial solid wastes, water used by industries, water from rivers and lakes, and seawater.

The tests were made following an ASTM standard [14] with some adaptations. A sodium sulphate solution was used, prepared as recommended by the standard [14]. The volume of the solution was at least five times the volume of the immersed specimens. The saturated solution of sodium sulphate covered the immersed specimens to a depth of at least 15 mm.

The procedure of the tests consists on cycles of immersion in the prepared solution of sodium sulphate for not less than 16 h nor more than 18 h. After the specimens were removed from the solution, permitted to drain for 15 ± 5 min, and placed in the drying oven. According the mentioned standard [14] the temperature of the oven shall have been brought previously to $110 \pm 5^\circ\text{C}$. The test of specimens with hydrophobic agents and coatings did not recommend the use of a temperature such high. So, the temperature of the oven in our tests was changed to the maximum of $50 \pm 5^\circ\text{C}$. The specimens were dried at this temperature until constant weight. After, the specimens were immersed again in the prepared solution of sodium sulphate.

After the production of the concretes, cubs with $100 \times 100 \times 100$ mm were moulded. The hydrophobic agent or the coatings were applied when the concrete had 28 days. Before applying the products the concrete specimens stayed 7 days outside water, in order to guarantee that the surfaces are not in wet conditions. The instructions of the supplier of the hydrophobic agent and coatings were followed during all the process. The tests occurred 7 days after products were applied on concrete specimens. A total of eight cycles was made. Analyze of sulphates attack was made by the weight variation along the cycles. Each value presented is the average of the weight variation of five specimens.

Figure 4 presents the mass losses at the end of the sulphates attack tests. The used silicone hydrophobic agent did not increase the protection against sulphate attack. The mass losses of the concretes with silicone hydrophobic agent (SIL I-A and SIL I-B) were higher than the mass losses of the unprotected concretes. The sulphate solution penetrated and as the cement is a non sulphate resistant the attack occurred. The used acrylic and epoxy coats (ACR I-A, ACR I-B, EP I-A and EP I-B) increased the protection against sulphate attack. The best performance was achieved with the epoxy coating concretes (EP I-A and EP I-B).

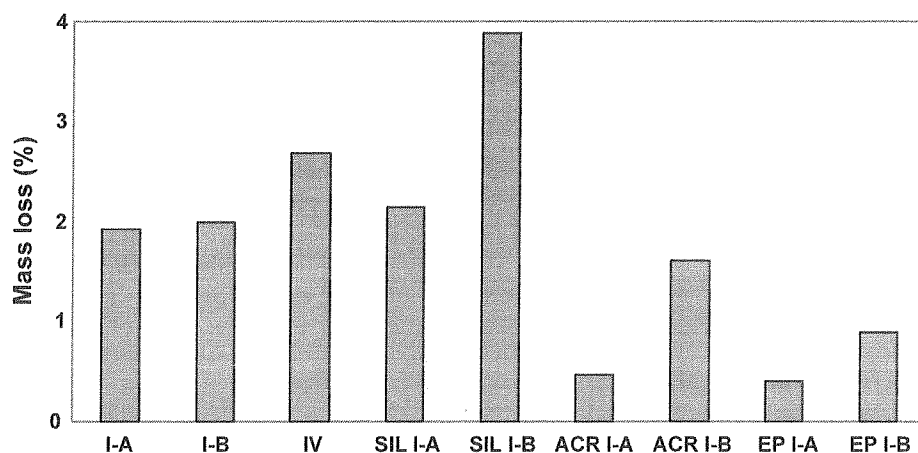


Figure 4. Mass losses for different concretes, hydrophobic agent and coatings.

The concretes without protection (I-A, I-B and IV) presented similar mass losses. The use of higher cement content and lower water-cement ratio (concrete I-B compared with concrete I-A) did not contribute to increase the performance against sulphate attack. Less porosity is also less space to accommodate expansions caused by reactions between sulphates and cement constituents. The concrete with cement IV did not solve the problem of sulphate attack because it can not be considered sulphate resistant cement. The C_3A content is too high, about 6.69 % (Table 2).

2.4 Acids and bases attack

The resistance of paintings to severe chemical attack was measured by exposition of one face to the test liquid following an European standard [15]. The specimens used on the test had the dimensions of 750x400x50 mm made as mentioned in another European standard [16]. The paintings were applied when the concrete had 28 days. Before applying coatings the concrete specimens stay 7 days outside water, in order to guarantee that the surfaces are not in wet conditions. The instructions of the supplier of the paintings were followed during all the process. The tests occurred 7 days after paintings were applied on concrete specimens.

The schema of the test consisted on putting eight PVC tubes $\varnothing 110 \times 30$ mm, on the specimen surface, when concrete is still fresh (Figure 5). Inside the tubes the solutions to be tested (acids and bases) were putted above the coated concretes, till a height of 10 mm. Two concretes were tested, I-A and I-B, in order to verify how coatings can perform on different concretes. The test liquids used were the following: H_2SO_4 (pH:-0.19) and NH_4OH (pH:11.87), with a concentration of 20% by volume. During the test the tubes were cover by a plastic film, in order to avoid the evaporation of test liquids.

The test has a duration of 28 days in accordance with [5]. Once a week the degradation of the specimens was analysed comparing with non tested specimens, if necessary the level of the test liquid was reposed. The results of blistering, cracking, flaking and chalking will be presented following ISO standards [17 - 20] that give methods for evaluation of the degrees of degradation of paintings (Figure 6). At the end of the exposition to the test liquids, adhesion tests were made following an ASTM standard [21] by pull-off method.

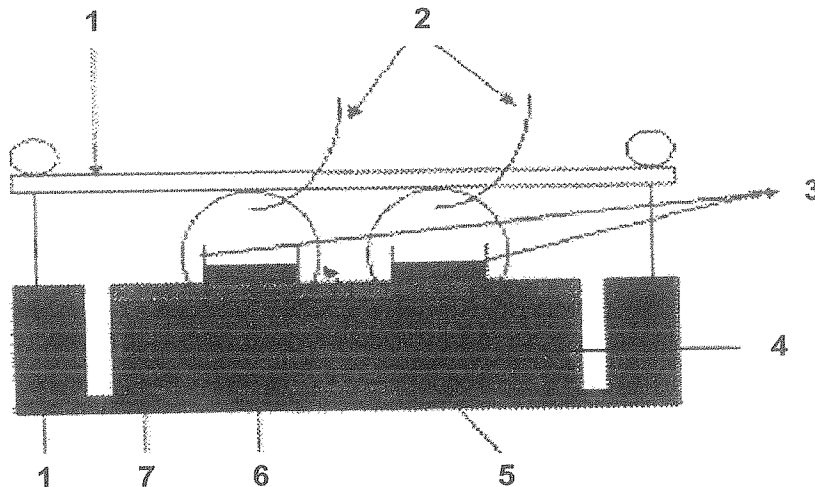


Figure 5. Schema of acids and bases attack test [1: Fixation base (used in pressure test), 2: Air compressed tube (pressure test), 3: Bonded tubes, 4: Concrete specimen, 5: Chamber (pressure test), 6 : Test liquid, 7: Painting, 8: Metallic ring].

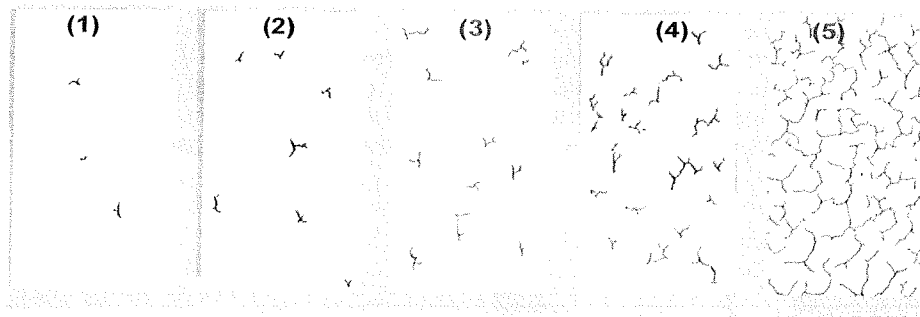


Figure 6. Photos to assessment the degree of cracking, no preferential direction (1, 2, 3, 4 and 5).

Tables 6 and 7 present the results of the tests and of the visual inspections made. The concretes coated with epoxy resin (EP I-A and EP I-B) presented better behaviour than concretes coated with acrylic resin (ACR I-A and ACR I-B), excepted for cracking and chalking parameters. The difference between acrylic and epoxy is important in adhesion after acid attack, with a bad behaviour for acrylic painting. The acid caused more degradation than the base. About acid attack there was a worst behaviour of coated concrete I-B (ACR I-B and EP I-B). This is due to the expansive reactions that occur between sulphuric acid and components of concrete. The low porosity of concrete I-B leave less space to accommodate these expansions and the degradations appear.

Table 6. Results of acid and base attack

References		Blistering		Cracking		Flaking	Chalking
Test liquid	Concrete	Dimension (Degree)	Surface (Degree)	Dimension (Degree)	Surface (Degree)	Degree	Degree
H ₂ SO ₄	ACR I-A	5	5	0	0	0	1
H ₂ SO ₄	ACR I-B	5	5	0	0	0	*
H ₂ SO ₄	EP I-A	3	3	4	2	0	2
H ₂ SO ₄	EP I-B	5	2	5	4	0	4
NH ₄ OH	ACR I-A	1	1	0	0	0	2
NH ₄ OH	ACR I-B	0	0	0	0	0	0
NH ₄ OH	EP I-A	0	0	2	1	0	1
NH ₄ OH	EP I-B	0	0	2	1	0	2

[Note] *: The test was not possible due to 100 % of blistering.

Table 7. Results of loss in adhesion strength after acid and base attack

References	Loss in adhesion strength (%)	
Test liquid	Concrete	
H ₂ SO ₄	ACR I-A	100
H ₂ SO ₄	ACR I-B	100
H ₂ SO ₄	EP I-A	8
H ₂ SO ₄	EP I-B	10
NH ₄ OH	ACR I-A	0
NH ₄ OH	ACR I-B	5
NH ₄ OH	EP I-A	0
NH ₄ OH	EP I-B	1

3 CONCLUSIONS

The performance of the used protected concretes against chemically aggressive environments was generally better than the performance of the unprotected concretes. The used epoxy coated concrete achieved the best results in all the chemical environments that include chlorides, sulphates, one acid and one base. The composition of the concretes is an important factor affecting performance against chemically aggressive environments. The unprotected and the protected concrete with higher cement content and lower water-cement ratio performed better than the others concretes, against penetration of chlorides, due to the less porosity. Related to sulphates and sulphuric acid attacks, unprotected and protected concretes that performed best, were made with the lower cement content and the higher water-cement ratio. The high porosity is good to accommodate expansions caused by reactions that occur during these attacks.

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