

1 **Corrosion rate of carbon steel in carbonated concrete – a critical review**

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11 **Keywords**

12 (C) Corrosion, Carbonation, Durability, Long-Term Performance – (D) Blended Cement

13

14 **Abstract**

15 Reinforced concrete with lower environmental footprint (lower CO<sub>2</sub> emission) can be  
16 obtained by reducing the clinker content in the cements. As the carbonation of concrete is  
17 faster, corrosion of steel in carbonated concrete during the propagation phase is becoming  
18 important both for science and practice. The present literature review summarises the state  
19 of the art, reporting corrosion rate data for a broad range of cement types, w/b ratios and  
20 environmental conditions. Correlations between corrosion rate and the main influencing  
21 parameters are elaborated and discussed. It confirms that the corrosion rate of steel in  
22 carbonated concrete is not under ohmic control. More important are the degree of pore  
23 saturation and the effective steel area in contact with water filled pores. It also emerges that  
24 the new blended cements have to be systematically studied with respect to the corrosion  
25 behaviour of steel in carbonated concrete in order to make reliable service life prediction.

26

27 **1. Introduction**

28 *1.1 Background*

29 Carbonation means the progressive neutralization of the alkaline constituents of concrete by  
30 carbon dioxide in the air forming mainly calcium carbonate. In this neutralized environment  
31 reinforcing steel is no more protected by the alkaline pore solution of fresh concrete. When  
32 the carbonated surface zone reaches the depth of reinforcing steel, significant corrosion may  
33 be initiated [1]. Indeed, corrosion of steel in carbonated concrete was a major concern of  
34 research and practice in the years from 1950 to 1990, a review of the published literature on  
35 carbonation and its effects was published by Parrot in 1987 [2]. The research findings led to  
36 the requirement of dense concrete (lower w/c ratio), the control of concrete properties and to

37 a marked increase in the cover depth (from 20 mm to 35 mm) in the codes of practice. The  
38 European standard on concrete EN 206-1 published in the year 2000 classified the risk of  
39 carbonation-induced corrosion depending on the severity of the environment (XC1 to XC4).  
40 With the minimum requirements given in the recommendations (maximum w/c ratio,  
41 minimum cement content, minimum cover depth) the codes of practice since then give  
42 guidance for reinforced concrete made with Portland cement (CEM I) on how to avoid  
43 carbonation induced corrosion for structures with expected service life of 50 or 100 years.

#### 44 *1.2 Carbonation of concrete*

45 The role of carbonation as a factor that contributes to the degradation of reinforced concrete  
46 is becoming increasingly important again for two reasons: first many old reinforced concrete  
47 structures that were built before modern standards were applied are ageing and have to be  
48 maintained. Secondly, the need to reduce CO<sub>2</sub> emission [3] and to obtain materials having a  
49 reduced environmental footprint, is leading to a reduction of the clinker content in the  
50 cements. Clinker (CEM I) is substituted with supplementary cementitious materials (SCM)  
51 such as limestone, fly-ash (FA), ground granulated blast-furnace slag (GGBS) etc. In the  
52 future, blended cements with increasingly lower clinker content and a huge variety of  
53 supplementary cementitious materials (SCM) will be used [4]. The future potential for  
54 application of blended cements depends on the current application level, on the availability of  
55 blending materials, and on standards and legislative requirements. The global potential for  
56 carbon dioxide emission reduction through producing blended cement is estimated to be at  
57 least 5% of total carbon dioxide emissions from cement making, but may be as high as 20%,  
58 the potential savings would vary by country, and even by region, according to local  
59 availability [5-8].

60 The introduction of low clinker binders has strongly reduced the pH buffer capacity as a  
61 result of the reduction (or elimination) of the calcium hydroxide reserve, considered one of  
62 the main reasons for the corrosion inhibiting nature of Portland cement systems [9].

63 Comprehensive reviews have summarized the effect of ground granulated blast-furnace slag  
64 (GGBS) [10] and fly ash (FA) [11] on the carbonation resistance of concrete. It is shown that  
65 FA and GGBS increase the carbonation rate of concrete. The influence of the cement type on  
66 carbonation rate was proposed to be contained in a single parameter termed “the effective  
67 buffering capacity of the cementitious binder expressed as an equivalent Portland cement  
68 content” [12]. This has been demonstrated by a recent work of Lehmann et al. [13] where the  
69 different blended cements could be rationalized by the CaO content. The carbonation rate of  
70 blended cements has been found to be a factor of 2 – 4 higher than for Portland cement [14,  
71 15], thus the recommendations in the standards based on the experience with Portland  
72 cement are no more applicable. For service life prediction of concrete structures with new,

73 blended cements, corrosion rate data are urgently needed because the so-called “corrosion  
74 propagation stage” might be a significant part of the total service life.

### 75 *1.3 Corrosion of steel in carbonated concrete*

76 Maximum rates of carbonation are observed when the concrete is exposed to atmospheres  
77 with relative humidity in the range from 55 – 75%. The corrosion rate of embedded steel in  
78 carbonated concrete in this humidity range is not of practical concern [1]. At conditions of  
79 high RH and especially by periodic wetting and drying the risk of corrosion increases  
80 markedly. The understanding of corrosion rates in carbonated concrete, in dependence of  
81 binder composition and mix design, is of major importance to provide adequate codes for  
82 ensuring long, maintenance free service life.

83 The service life of concrete structures made with ordinary Portland cement can be predicted  
84 from the air permeability and corrosion rate determinations [16-18]. However, mechanistic  
85 understanding is still lacking, not allowing us to deduce a quantitative model in the case of  
86 blended cements, particularly because we do not know well how these binders age [19].  
87 Another reason for this lack of a quantitative model is that, in most cases, the test results are  
88 not comparable due to the enormous variety of local SCMs [20], resulting in dozens of  
89 different blended cements, experimental approaches, in terms of sample design and  
90 corrosion measuring techniques.

91 In this paper a number of publications addressing the topic of carbonation-induced corrosion  
92 is critically reviewed [21-73] in order to understand the magnitude of the problem, the main  
93 influencing parameters and the probable mechanism of the process.

94

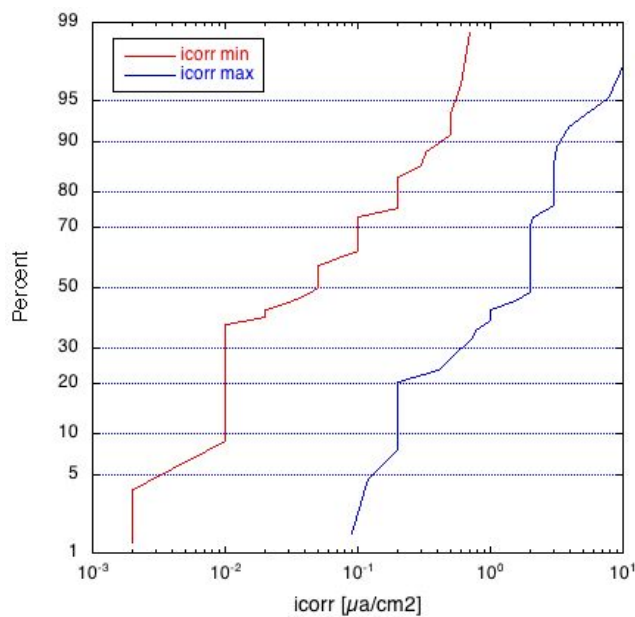
## 95 **2. Literature data on corrosion rate of steel in carbonated concrete**

96 Compared to the several hundred reports and papers regarding the resistance to carbonation  
97 of mortars and concretes made with different (blended) cements, only about 50 publications  
98 have been identified that refer to the corrosion rate of reinforcing steel in carbonated con-  
99 crete in the last 35 years (1980 – 2016). Table 1 summarizes all the publications considered  
100 in the present evaluation. The corrosion rate data were obtained from a variety of  
101 experimental setups and the corresponding details are reported in the table.

102 The majority of data (40 out of 53) stems from laboratory studies. Several authors [30, 43, 45,  
103 47, 53, 55, 60, 71] report corrosion rate data from carbonated structures, mainly buildings, or  
104 from final phase of long-term field tests intended to study carbonation behavior [24, 29, 45,  
105 47]. These papers state “practical exposure conditions” but details on changes of the  
106 temperature are given by only one paper [60] and changes in relative humidity are presented

107 only in two publications [47,60], thus the results of these field tests are more difficult to  
 108 interpret.

109 From most of the works it was possible to extract a minimum and a maximum value of the  
 110 corrosion rate (Table 1). From this global perspective, a large overall scatter is apparent: the  
 111 reported values range from 0.002  $\mu\text{A}/\text{cm}^2$  [23] to 20  $\mu\text{A}/\text{cm}^2$  [41], thus over four orders of  
 112 magnitude. Comparing the cumulative distribution of these values (Figure 1) the average  
 113 value of the minimum corrosion rate is about 0.08  $\mu\text{A}/\text{cm}^2$ , the average of the maximum is  
 114 about 2  $\mu\text{A}/\text{cm}^2$ . The large scatter in literature is related to different experimental procedures  
 115 and to the parameters that affect corrosion rate of steel in carbonated concrete; this will be  
 116 discussed in the following sections.



117  
 118 Figure 1: Cumulative probability distribution of the minimum and maximum corrosion rate  
 119 reported in literature (see Table 1).

120  
 121 Table 1 Compilation of literature work analyzed and discussed in this review.

	Binder (materials)	w/b	Carbonation (CO <sub>2</sub> %)	Exposure	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Test method
Gonzales et al. 1980 [21]	OPC	0.5	100%	Cycles: 50% RH 100% RH PI	0.03 - 2	LPR
Gonzalez et al. 1983 [22]	SRPC, SL, PZZ, FA	0.5	100%	ID	0.1 – 0.4	LPR
Molina et al. 1985 [23]	OPC	0.5	/	40% RH 100% RH	0.002	LPR
Nagataki et al. 1986 [24]	OPC FA	0.5 0.6	Natural	OD		VI
Alonso and Andrade 1987 [25]	OPC, SRPC, SL, PZZ, FA	0.5	100%	Cycles: 50% RH 100% RH	0.01 - 10	LPR

				PI		
<b>Alonso et al. 1987 [26]</b>	SRPC, PZZ, FA	0.5	100%	Cycles: 50% RH, 100% RH PI	0.01 - 10	LPR
<b>Alonso et al. 1988 [27]</b>	OPC, SRPC, SL, PZZ, FA	0.5	100%	Cycles: 50% RH, 100% RH PI	0.01 - 10	LPR
<b>Menzel 1988 [28]</b>	OPC	0.7	100%	Wet-dry PI	0.1 - 3	MC
<b>Kokubu and Nagataki 1989 [29]</b>	OPC, FA		Natural	OD		VI
<b>Sergi et al 1990 [30]</b>	OCP	?	Natural	Wet-dry	0.05 – 0.2	LPR
<b>Collepari et al. 1990 [31]</b>	OCP, FA, PZZ	0.35 0.5 0.65 0.8	30%	75% RH 90% RH		LPR
<b>Short et al. 1991 [32]</b>	OPC, SL, FA	0.9	Natural	40% RH 60% RH 75% RH 90% RH	0 - 2	LPR
<b>Glass et al. 1991 [33]</b>	OPC	1	5%	40% RH 60% RH 75% RH 90% RH	0.02 - 0.9	LPR
<b>Dhir et al. 1992 [34]</b>	OPC, FA		4%	55% RH 75% RH 95% RH Cycles	0.05 - 2	LPR
<b>Branca et al. 1992 [35]</b>	OPC, FA	0.35 0.50 0.65	30%	75% RH	No corrosion	LPR
<b>Haque and Kawamura 1992 [36]</b>	OPC FA	0.45	Natural	OD		HCP
<b>Lopez and Gonzalez 1993 [37]</b>	OPC	0.5	Natural	>90% RH 50% RH	0.01	LPR
<b>Parrott 1994 [38]</b>	OCP, SL, FA, LS	0.35 0.47 0.59 0.71 0.83	Natural	ID OD ODS PI	0.01 – 18	WL
<b>Cao et al. 1994 [39]</b>	OPC FA	0.6	4%	50%	0.1 – 1.3	LPR
<b>Anastasia et al. 1995 [40]</b>	OPC	0.65 0.56 0.47	/	70% RH 90%RH IM	0.01 – 5	LPR
<b>Parrott et al. 1996 [41]</b>	OCP, SL, FA, LS	0.59	Natural	PI	0.6 - 20	WL
<b>Olsen et al. 1997 [42]</b>	OPC, SL	0.49 0.54 0.78 0.89	Natural	OD	% Corrosion loss	WL
<b>Saguez et al. 1997 [43]</b>	Existing structures OPC, SL, FA	Lab: 0.37 0.5	5%	100% RH	0.2 - 0.6 Field 0.2 – 4 Lab	LPR EIS GST
<b>Moreno and</b>	OPC, FA	0.37	4%	60% RH	/	LPR

<b>Saguez 1998 [44]</b>		0.50				
<b>Casto Moreno et al 1999 [45]</b>	Existing structures Lab specimens	0.7 0.53 0.5 0.46	Field tests	OD	0.005 – 0.2	LPR
<b>Dunster et al. 2000 [46]</b>	CAC	0.4 0.6 0.8	10%	65% RH 75% RH 95% RH OD	0.008 - 3	LPR
<b>Sergi et al. 2000 [47]</b>	Structures	/	Natural	ODP	0.01- 6	LPR
<b>Millard et al 2001 [48]</b>	OPC	/	/	60% RH 90% RH	0.5 – 2	LPR
<b>Chi et al. 2002 [49]</b>	OCP SL	0.58 0.48	50% 75% 100%	3.5% NaCl		EIS HCP
<b>Montemor 2002 [50]</b>	OPC FA	0.6	5%	65% RH		EIS
<b>Americo and Nepomuceno 2003 [51]</b>	OPC	0.6	Natural	Cycles wet-dry 100%	0.02 - 3	LPR
<b>Moreno et al. 2004 [52]</b>	OPC LS	0.55 0.62 0.7 0.8	4%	ID 100% RH	0.01 – 1	LPR
<b>Varjonen 2004 [53]</b>	OPC From structures	1.08 0.74	0.04% 4%	75% RH 97% RH PI	0.01 – 6	LPR
<b>Smith et al. 2004 [54]</b>	OCP, MS, SL, FA	0.43	/	ID	0.1 - 0.73	LPR
<b>Moreno et al. 2005 [55]</b>	From structures	/	/	OD		HCP
<b>Moreno et al. 2005 [56]</b>	OCP LS	0.65 0.74 0.85	4%	80% RH >90% RH	0.002 - 2	LPR HCP
<b>Baccai et al. 2006 [57, 58]</b>	OPC, ESPC, SL	0.55	15%	90%RH	0.2 - 1	EIS
<b>Medagoda et al. 2008 [59]</b>	OPC, FA, SL	0.55	4%	95% RH	0.7 - 2.1	LPR
<b>Mattila and Pentti 2008 [60]</b>	Real structures	/	4%	OD ODS ID	0.05 - 1	LPR
<b>Zornoza et al. 2009 [61]</b>	OPC, FA, CC	0.4	100%	100% RH	0.06 - 0.2	LPR WL
<b>Kulakowski et al. 2009 [62]</b>	OPC SF	0.40 0.55 0.7	>50%	70% RH	0.01 - 0.12	LPR
<b>Dinakar et al. 2009 [63]</b>	OCP FA	0.3	Natural	/	0.1 – 1.5	TE
<b>Garces et al. 2010 [64]</b>	OPC FA	0.5 0.7	100%	65% RH	0.3 - 0.5	LPR
<b>Arredondo-Rea et al. 2012 [65]</b>	OPC, RCA, FA, SF	0.48	6%	70% RH	0.07 – 0.2	LPR
<b>Kujur J. 2012 [66]</b>	OPC, PZZ, SL	0.45 0.5 0.55	4%	Not found	Not found	LPR
<b>Page C.L. 2012 [67]</b>	Review					
<b>Andrade et al. 2013 [68]</b>	OPC, WC, SL, FA	0.5	100%	IM	0.33 - 3.2	LPR
<b>Chavez-Ulloa et al. 2013 [69]</b>	OPC	0.5 0.7	Natural 3%	65% RH 90% RH	0.01 - 0.2	EIS

				ODS		
<b>Gurdian et al. 2014 [70]</b>	OPC, CC, FA	0.45	100%	50% RH	0.2 - 0.6	LPR
<b>Aligizaki K.K. 2014 [71]</b>	Structures, OPC, FA, SL	/	Natural	OD ODS	/	
<b>Castel and Nasser 2015 [72]</b>	OPC	0.45	50%	65% RH	0.5 - 2	LPR WL MC
<b>Aguirre et al. 2016 [73]</b>	OPC, MK, SF	0.55	1%	65% RH	0.05 – 2	LPR EIS

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124

125

126 Table 2: Abbreviations used in this review.

Materials		Exposure		Test Method	
Ordinary Portland Cement	OPC	Relative Humidity	RH	Linear Polarization Resistance	LPR
Sulphate Resistant Portland Cement	SRPC	Partial Immersion	PI	Electrochemical Impedance Spectroscopy	EIS
Blast Furnace Slag	SL	Immersion	IM	Weight Loss	WL
Fly Ash	FA	Outdoor	OD	Half Cell Potential	HCP
Natural Pozzolans	PZZ	Outdoor Sheltered	ODS	Macrocell Current	MC
Limestone	LS	Outdoor Partially Sheltered	ODP	Visual Inspection	VI
Calcium Aluminate Cement	CAC	Indoor	ID	Galvanostatic Step Technique	GST
Early Strength Portland Cement	ESPC			Tafel Extrapolation	TE
Cracking Catalyst	CC				
Recycled Concrete Aggregates	RCA				
White Cement	WC				
Metakaolin	MK				
Silica Fume	SF				

127

## 128 2.1 Experimental setups

129 Most of the works cited in this review refer to laboratory conditions [21-23, 25-28, 31-44, 46,  
130 48-54, 56-59, 61-70, 72, 73]. The experimental setup was mainly mortar or concrete  
131 specimens of different geometries, with a minimum characteristic dimension (smallest side or  
132 diameter of the specimen) of 2 cm [21, 22, 25-27, 37, 61, 64, 68] up to 18 cm [32, 33] with  
133 embedded reinforcing steel with diameter starting from 0.6 cm up to 1 cm. In Table 3 the  
134 different geometries and cover depths used are reported. Prisms are the most common  
135 geometry and the cover depth spans over a range dictated by the different intentions of the  
136 authors: 0.4 – 0.9 cm were used for fastest carbonation process, 2.0 – 2.9 cm were used as  
137 compromise between fast carbonation and realistic conditions. Few works, in order to have a  
138 more ideal system (surface condition and area), used steel sheets, either embedded in  
139 mortar layers [28,39] or used as a substrate on which the mortar was applied [53].

140

141 Table 3: Sample geometry and cover depth used in the different literature works cited.

Shape	Cover (cm)	Reference	Total
<b>Cylinder</b>	0.4-0.9	60	1
	1.0-1.9	40, 60, 73	3
	2.0-2.9	24, 29, 40, 45	4
	3.0-5.0	24, 29, 63, 70	4
<b>Prism</b>	0.4-0.9	21-23, 25-28, 37, 39, 61, 68	11
	1.0-1.9	36, 42, 50, 51, 54, 57, 58, 69, 72	9
	2.0-2.9	31, 35, 36, 42, 43, 44, 51, 52, 53, 56, 57, 58, 69	13
	3.0-5.0	31, 35, 62, 69	4
<b>Cube</b>	0.4-0.9	38, 41	2
	1.0-1.9	32, 38, 51, 56	4
	2.0-2.9	33, 34, 38, 51, 56	5
	3.0-5.0	59	1

142

143 2.2 Measurement methods

144 In most papers (37 out of 53) the corrosion rate of steel in carbonated mortar or concrete  
 145 was determined from polarization resistance measurements (Table 4). Other methods such  
 146 as weight loss or impedance were also used; in some works two [61, 66, 73] or even three  
 147 [43, 72] different methods were used and the results were compared. Two papers compared  
 148 LPR with weight loss [61, 72] and concluded that the corrosion rates calculated from the two  
 149 methods are in good agreement, within 20% of relative variation. In some works only  
 150 qualitative evaluation of the surface state was carried out, with no real corrosion rate  
 151 reported, using either half-cell potential measurements or simple visual inspection of the  
 152 steel surface (Table 4).

153

154 Table 4: Measurement methods to determine the corrosion rate used in the different  
 155 literature works cited.

Method	Reference	Total no. of publications
<b>Linear Polarization Resistance (LPR)</b>	21-23, 25-27, 30-35, 37, 39-40, 43-48, 51-54, 56, 59-62, 64-66, 68, 70, 72, 73	37
<b>Electrochemical Impedance Spectroscopy (EIS)</b>	43, 49, 50, 57, 58, 69, 73	7
<b>Weight Loss (WL)</b>	38, 41, 42, 61, 72	5
<b>Half Cell Potential (HCP)</b>	36, 49, 55, 56	4
<b>Macrocell current (MC)</b>	28, 72	2
<b>Visual Inspection (VI)</b>	24, 29	2
<b>Galvanostatic Step Technique</b>	43	1



156

157 2.3 Relevance

158 Table 1 summarizes the main experimental parameters and minimum/maximum corrosion  
159 rates measured by the respective authors in the reviewed studies. However, when evaluating  
160 the literature – i.e. assessing trends, general agreements, and controversial issues (compare  
161 the following sections) – we do not consider all studies equally relevant. Many papers cited  
162 studied the carbonation process, data on corrosion in carbonated concrete were more a side  
163 effect and obtained from visual inspection [24, 29] or half cell potential measurements [36,  
164 55] and were thus not considered in the further evaluation. Also data on galvanized steel [56]  
165 and carbonation in presence of chlorides [44, 45] were not included.

166

**167 3. Influencing parameters**

168 Some of the differences observed in corrosion rates of steel in carbonated concrete reported  
169 in the literature may be related to the different experimental procedures regarding curing,  
170 carbonation and conditioning of the samples under test. The main parameters that influence  
171 the corrosion rate of steel in carbonated mortar and concrete are the exposure conditions,  
172 the type of binder and the water/binder ratio [1, 2] as will be discussed below.

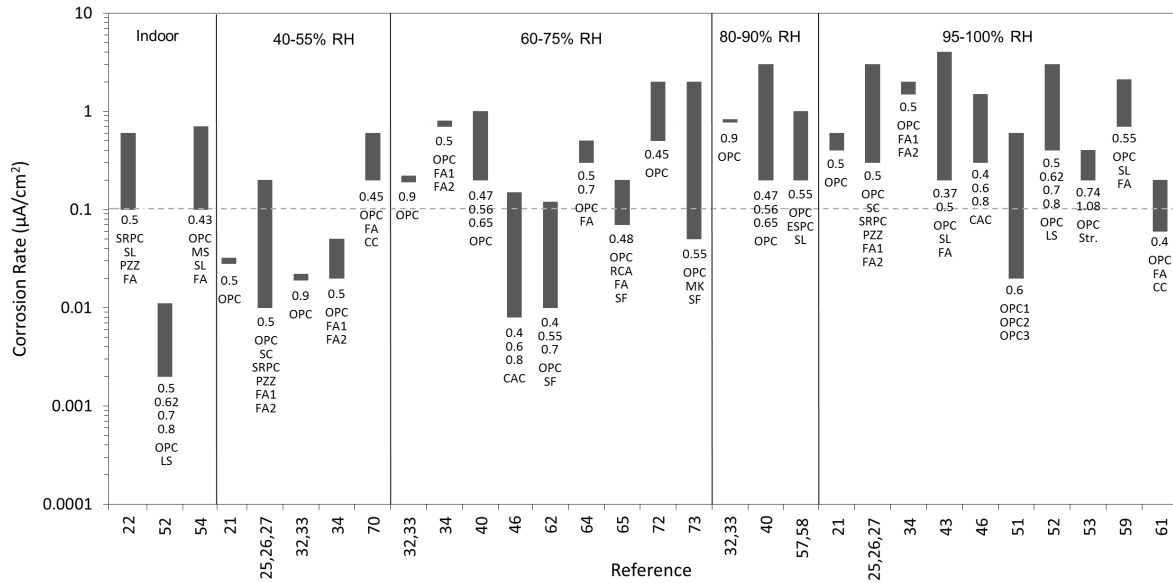
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**174 3.1 Exposure conditions – relative humidity (XC3)**

175 Atmospheric exposure conditions with varying relative humidity are frequently encountered  
176 inside buildings or in sheltered conditions outside and are thus of great practical relevance.  
177 The relative humidity (RH) studied in the reported publications spans over a wide range from  
178 40% to 100%. Many works (16) studied the corrosion of steel in carbonated concrete in the  
179 range from 60% to 75% RH [31-35, 40, 44, 48, 50, 53, 62, 64, 65, 69, 72, 73], the reason is  
180 that in most of the studies the carbonation was carried out in this humidity range and  
181 corrosion rate monitoring was performed during the process itself. 15 papers reported refer  
182 to the high humidity range (95% to 100%) [21, 23, 25-27, 34, 37, 43, 44, 51-53, 56, 59, 61].

183 A number of publications studied the corrosion behavior of embedded steel only at one  
184 single constant relative humidity [35, 39, 43, 44, 50, 51, 57, 58, 59, 61, 62, 64, 65, 70, 72, 73].  
185 Others carried out a comparison between different constant RH conditions [21, 23, 25, 26,  
186 31-34, 37, 40, 44, 48, 52, 53, 56, 69]. Finally, perhaps more realistically, some studies  
187 focused on actual environmental XC3 exposures, either indoor [22, 38, 44, 46, 52, 54, 60] or  
188 outdoor [38, 46, 60, 71].

189 In Figure 2 the minimum and maximum corrosion rates reported in the different RH regimes  
 190 are presented. Studies referring to half-cell potential or EIS data and studies involving the  
 191 presence of chlorides are not included. As a general trend an increase of the corrosion rate  
 192 with higher relative humidity in the environment can be noted. The mean values suggest that  
 193 there is an increase of almost one order of magnitude from exposure to ~50% RH (0.02 - 0.4  
 194  $\mu\text{A}/\text{cm}^2$ ) to exposure to ~95% RH (0.08 - 3  $\mu\text{A}/\text{cm}^2$ ). The values in 95 – 100% RH correspond  
 195 to 5 – 20  $\mu\text{m}/\text{year}$  loss of cross section and are significant.



196  
 197 Figure 2: Compilation of the reported minimum and maximum corrosion rate values of steel  
 198 in carbonated mortar or concrete in different exposure conditions (RH) corresponding to XC3.  
 199 For each literature reference the w/b ratio(s) and the binder(s) studied are indicated.

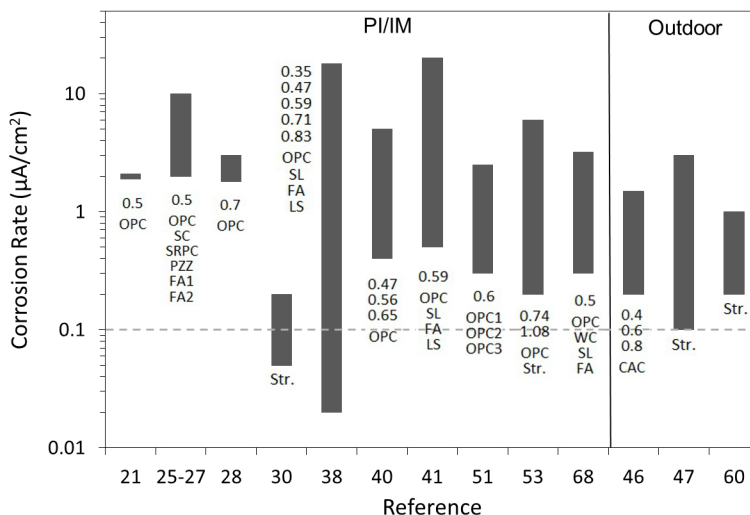
200  
 201 3.2 Exposure conditions – wet/dry cycling (XC4)

202 Many papers (21) studied the corrosion rate of steel in carbonated mortar or concrete in  
 203 exposure class XC4 [21, 24-30, 36, 38, 40-42, 45, 46, 51, 53, 55, 60, 68, 69, 71]. Minimum  
 204 and maximum corrosion rate values reported for partially or fully immersed conditions and  
 205 outdoor exposure are presented in Figure 3. In all studies the maximum corrosion rate values  
 206 reported are higher than 1  $\mu\text{A}/\text{cm}^2$  (except ref. [30] where samples from real structures were  
 207 studied), in few cases  $i_{\text{corr max}}$  is found even higher than 10  $\mu\text{A}/\text{cm}^2$ . The variability of almost a  
 208 factor 1000 reported [38] is due to the fact that many different variations were studied in  
 209 terms of w/b ratio (5 different), binder type (4 different) and the use of as received or pre-  
 210 cleaned steel bars that cannot be identified precisely from the original data.

211 Exposure class XC4 implies direct contact of the specimen with water for a certain time, but  
 212 the studies reported show quite a large variability in terms of duration of the wet phase: two  
 213 works [38, 53] carried out the tests by partial immersion of the specimens (6 hours [38], 7

214 days [53]) followed by 28 days of exposure to 97-100% RH to maintain a high humidity  
 215 condition and promote active corrosion. Seven publications [21, 25-27, 40, 41, 68] used a  
 216 partial or fully immersed condition for long time (14 days [68] to 1 year [40]) without  
 217 attempting to reproduce realistic wet-dry cycles. Data published by Alonso et al. [25-27] refer  
 218 to at least 2 wet/dry cycles per sample but each exposure condition varied between 20 and  
 219 200 days. Only three studies applied an actual multiple wet-dry testing [28,30,51], meaning  
 220 that the samples were put in contact with water for a predetermined amount of time (variable  
 221 between 8 hours [28] and 7 days [51]) and then let to dry in low RH environment, after which  
 222 the procedure was repeated.

223 In total 9 publications refer to outdoor exposure (table 1), but in four papers the evaluation  
 224 was only qualitative, e.g. by visual inspection [24, 29] or by monitoring of the corrosion  
 225 potential [36, 55]. Other papers were not included because of the presence of chloride ions  
 226 (marine environment) [45], because only the carbonation process itself was considered [71]  
 227 or because only the percentage of average corrosion loss was reported [42]. Three papers  
 228 show quantitative data related to carbonation-induced corrosion in outdoor conditions [46, 47,  
 229 60]. Comparison between laboratory specimens in contact with water and outdoor exposure  
 230 condition is difficult as for outdoor conditions no data regarding the amount or frequency of  
 231 precipitations are reported. Laboratory wet specimens show a substantially higher corrosion  
 232 rate than real outdoor exposure measurements, most likely because of the fraction of wet  
 233 time that is shorter in the case of outdoor exposure than in well-controlled laboratory cyclic  
 234 wetting/drying exposure.

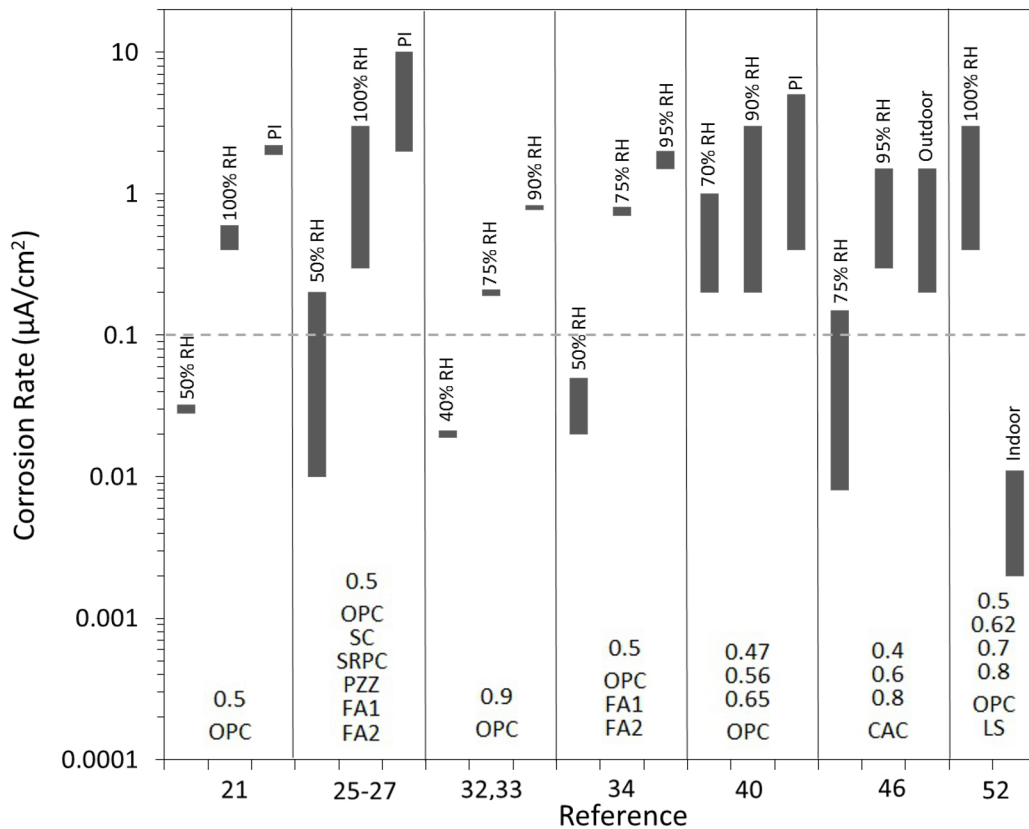


235  
 236 Figure 3: Compilation of the minimum and maximum corrosion rate of steel in carbonated  
 237 mortar or concrete in exposure conditions that imply contact with liquid water (XC4). For  
 238 each literature reference the w/b ratio(s) and the binder(s) studied are indicated.

239

### 240 3.3 Summary on the influence of exposure conditions

241 The situation regarding the influence of exposure conditions becomes clearer when the  
242 evaluation is limited to those publications [21, 25-27, 32-34, 40, 44, 46, 52] reporting  
243 corrosion rate values measured at different RH / water contact / real environment, but in the  
244 same experimental conditions (Fig. 4). A factor of up to nearly 100 in corrosion rate can be  
245 found within the same publication when changing the exposure condition from 50% RH to  
246 partially immersed [21, 25-27] or from 50% RH to 95% RH [32 – 34]. Contact with liquid  
247 water leads to corrosion rates from 2 to 4 times higher than in high humidity environment  
248 (from 95-100% RH, 0.38-1.76  $\mu\text{A}/\text{cm}^2$ , to PI/IM, 0.75-7  $\mu\text{A}/\text{cm}^2$ ). All the papers report  
249 consistently higher corrosion rates in exposure class XC4 suggesting that contact with water  
250 is the most aggressive condition in terms of carbonation induced corrosion.



251

252 Figure 4: Summary of corrosion rate data from literature works studying the influence of  
253 different exposure conditions (immersed, constant RH, outdoor and indoor). For each  
254 literature reference the w/b ratio(s) and the binder(s) studied are indicated.

255

256 The large variability observed in the corrosion rate data reported in figure 4 *within* a single  
257 exposure condition [25-27, 40, 46] can be related to different mixes (binder type, w/b ratio)  
258 tested as is shown in the following two sections.

259

260 3.4 Type and amount of supplementary cementitious material

261 The corrosion rate of reinforcing steel in carbonated mortar or concrete has been studied in  
262 many works only for Ordinary Portland Cement (CEM I) [21, 23, 28, 30, 33, 37, 50, 58, 51-53,  
263 55, 69, 72]. CEM I has also been used in almost all the studies as reference material (Table  
264 5). From Table 5 it can further be seen that the second most studied binder is Fly Ash, the  
265 next frequently studied binder is Blast Furnace Slag, whereas Natural Pozzolans, Limestone  
266 or Silica Fume are studied rarely. The main finding reported by the authors is that the  
267 corrosion rate of steel in carbonated mortar or concrete increases for clinker replaced  
268 binders [22, 25-27, 34, 41-44, 58, 59, 61, 62, 65, 68, 70].

269

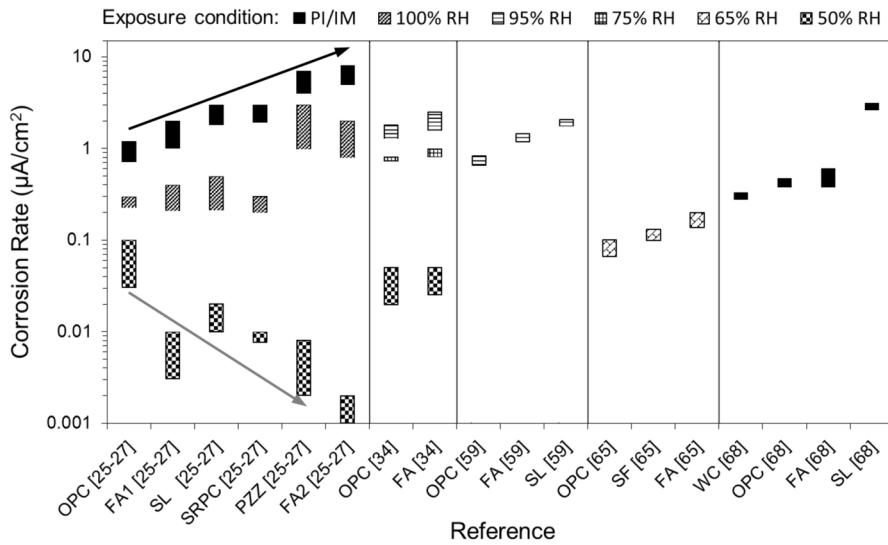
270 Table 5: Summary of the different binders used in the cited works.

<b>Materials</b>	<b>Reference</b>	<b>Total no. of publications</b>
<b>OPC</b>	21-25, 27-44, 48-50, 52-54, 56-59, 61-65, 66, 68-73	45
<b>Fly Ash</b>	22, 24, 25, 26, 27, 29, 31, 32, 34-36, 38, 39, 41, 43, 44, 50, 54, 59, 61, 63-65, 68, 70, 71	26
<b>Blast Furnace Slag</b>	22, 25, 27, 32, 38, 41-43, 49, 54, 57-59, 66, 68, 71	16
<b>Natural Pozzolans</b>	22, 25, 26, 27, 31, 66	6
<b>Limestone</b>	38, 41, 51, 52, 56	5
<b>Silica Fume</b>	62, 65, 73	3
<b>Sulphate Resistant Cement</b>	25, 26, 27	3
<b>Fluid Cracking Catalyst Residue</b>	61, 70	2
<b>Calcium Aluminate Cement</b>	46	1
<b>Microsilica</b>	54	1
<b>Metakaolin</b>	73	1

271

272 Studies that compare the influence of different type and amount of blended materials under  
273 identical experimental conditions are rare [25-27, 34, 59, 65, 68], the results are summarized  
274 in Figure 5. In the work by Alonso et al. [25-27] 6 binders in 3 different exposure conditions  
275 (50% RH, 100% RH and partially immersed) were tested. A study by Medagoda et al. [59]  
276 reports corrosion rates in carbonated specimens made with for OPC, fly ash and slag at 95%  
277 relative humidity. Parrott [38, 41] tested the carbonation process of a large variety of binder  
278 and w/b ratio combinations (37). Weight loss measurements at the end of the testing period

279 showed an increase of the steel corrosion rate for clinker replaced binders and for higher  
 280 clinker substitution, provided the same SCM was used.



281

282 Figure 5: Reported corrosion rate values (interval min – max) of steel in carbonated mortar or  
 283 concrete made with different binders exposed to different environments.

284

285 *Influence of the binder type*

286 In moist climates, generally higher corrosion rates can be observed in blended cements  
 287 compared to pure OPC, the latter showing the lowest corrosion rates among all binders  
 288 (Figure 5). This increase in corrosion rate with clinker substitution is very significant (more  
 289 than a factor 5) for partially or fully immersed conditions [25-27, 68]. In the humidity range  
 290 from 95% RH [34, 59] to 65% RH [65] a modest increase in corrosion rate with clinker  
 291 replacement is observed. At low relative humidity (50%) the corrosion rate in all samples is  
 292 very low (<0.1 µA/cm<sup>2</sup>) and the effect of clinker substitution is opposite:  $i_{corr}$  is highest for  
 293 OPC and decreases with clinker substitution [25-27].

294

295 *Influence of the amount of SCM*

296 Studies that analyzed the influence of the replacement level are rare [34, 41, 43, 44, 62], and  
 297 in two of them [34, 41] the influence of the substitution percentage cannot be clearly  
 298 determined because the data sets are overlapping in the graphs presented, but a tendency  
 299 to higher corrosion rates for higher clinker substitution can be found. Sagues et al. [43] found  
 300 corrosion rates 26% higher when increasing the fly ash content from 20% to 50% in  
 301 exposure condition XC3 (100% RH). Kulakowski et al. [62] studied the influence of silica  
 302 fume content (0%, 10% and 20%), the addition seemed to lead to no change in the corrosion

303 rate at w/c ratio of 0.4, but at w/c ratios of 0.55 and 0.7 the silica fume addition causes an  
304 increase of the corrosion rate from 20% to 100% higher than the reference pure OPC.

305

### 306 3.5 Influence of the water/binder ratio

307 Most of the experiments have been performed at constant water/binder (w/b) ratio, usually  
308 between 0.4 and 0.6. Some authors studied w/b ratios of 0.9 [32] or 1.0 [33] in order to  
309 enhance the transport properties and facilitate carbonation. Several publications investigated  
310 the influence of w/b ratio on the corrosion rate [31, 35, 38, 40, 42-44, 52, 56, 62, 66]. As a  
311 general trend of the results it can be concluded that a decrease in w/b ratio corresponds to a  
312 reduction in corrosion rate of the embedded steel in carbonated mortar or concrete, for  
313 example a decrease of w/b from 0.8 to 0.55 led to a decrease from  $2 \mu\text{A}/\text{cm}^2$  to  $0.8 \mu\text{A}/\text{cm}^2$   
314 ( $\sim 2.5$  times), at 100% RH in [52]. Other work did not find a statistically relevant influence [40,  
315 52, 56] or the data are difficult to extract from the graphs presented [38]. In few works the  
316 conclusions are disturbed by the experimental procedure [31, 35, 43].

317 In some studies a significant influence of the w/b ratio on the corrosion rate of steel in  
318 carbonated mortar was found at high RH [31, 44, 52]. At low RH the influence of the w/b ratio  
319 on the corrosion rate is negligible, suggesting that in low moisture condition the corrosion is  
320 so slow that the w/b ratio does not play an important role.

321

### 322 3.6 Influence of the carbonation condition

323 As most of the studies refer to laboratory work, very often an accelerated carbonation  
324 procedure has been applied (Table 6). The  $\text{CO}_2$  content in the carbonation chamber ranges  
325 from 0.03%  $\text{CO}_2$  (natural conditions) to 100%  $\text{CO}_2$ . The influence of the  $\text{CO}_2$  content during  
326 the carbonation phase on the corrosion rate of the embedded steel has not been studied; the  
327 works using different  $\text{CO}_2$  concentrations [49, 50, 69] only evaluate the differences in terms  
328 of carbonation propagation. In recent works the use of natural carbonation for corrosion  
329 studies became more and more rare, probably due to the long time needed for carbonation  
330 to reach the embedded steel, to the wider availability of carbonation chambers, and to the  
331 publication of studies showing negligible differences in changes in the microstructure due to  
332 carbonation for  $\text{CO}_2$  concentration up to 4% [13, 74, 75].

333 The relative humidity used for carbonation in controlled environment ranges from 55% to  
334 70%, known as the window for maximum carbonation rate. In the publications reported in this  
335 review there is almost no data on the influence of conditions of carbonation on the corrosion  
336 rate in carbonated mortar or concrete. Only Varjonen [53] reported corrosion rate values of

337 steel embedded in different types of specimens carbonated in presence of a CO<sub>2</sub>  
 338 concentration of 0.04% or 4%; the results showed a higher corrosion rate for specimens  
 339 carbonated in natural conditions (0.04%), approximately of a factor 1.5 with respect to the  
 340 specimens that underwent accelerated carbonation.

341 Table 6: Summary of the CO<sub>2</sub> concentration used in the carbonation process

<b>Carbonation</b>	<b>CO<sub>2</sub> (%) concentration</b>	<b>Reference</b>	<b>Total no. of publications</b>
<b>Natural</b>	0.03	24, 29, 30, 36-38, 40-42, 45, 47, 50, 51, 53, 55, 63, 69, 71	18
<b>Accelerated</b>	0.5-6	33, 34, 39, 43, 44, 50, 52, 53, 56, 59, 60, 65, 66, 69, 73	15
	6-99	31, 46, 49, 58, 62, 72	6
	100	21, 22, 25-28, 48, 49, 61, 64, 68	11

342

### 343 3.7 Other possible influencing parameters

344 Many other parameters can influence the measured corrosion rate. However, their influence  
 345 can hardly be quantified in the here reviewed publications, mostly due to a lack of reported  
 346 experimental details. Some examples:

- 347 • Temperature: the impact of different temperatures have been studied in only 2  
 348 publications [57, 58] (from the same authors and same data). The results are in  
 349 agreement with generally known laws of chemical processes, higher corrosion rate at  
 350 higher temperatures;
- 351 • Type of embedding material: the samples were made either by mortar or concrete,  
 352 while cement paste was never used; no statistically relevant difference in corrosion  
 353 rate was noticed in the considered studies;
- 354 • Steel surface treatment: unfortunately, the reviewed publications did not give details  
 355 about steel surface treatments (such as cleaning, degreasing, sandblasting, etc.).
- 356 • Electrochemical measuring technique: the test method used to determine corrosion  
 357 rates can influence the results [76]. LPR can overestimate the corrosion rates in a  
 358 magnitude dependent on the potential scan rate, on the other hand weight loss  
 359 measurements are affected by the mechanical procedure of rebar removal and  
 360 surface cleaning. As a matter of fact, the highest corrosion rates found are measured  
 361 by means of weight loss measurements [38, 41].



362 • Method of accelerating carbonation: from an experimental point of view the specific  
363 carbonation conditions can have an influence on the corrosion rate results,  
364 unfortunately no data are available in this respect and further study is needed.

#### 365 **4. Correlations observed**

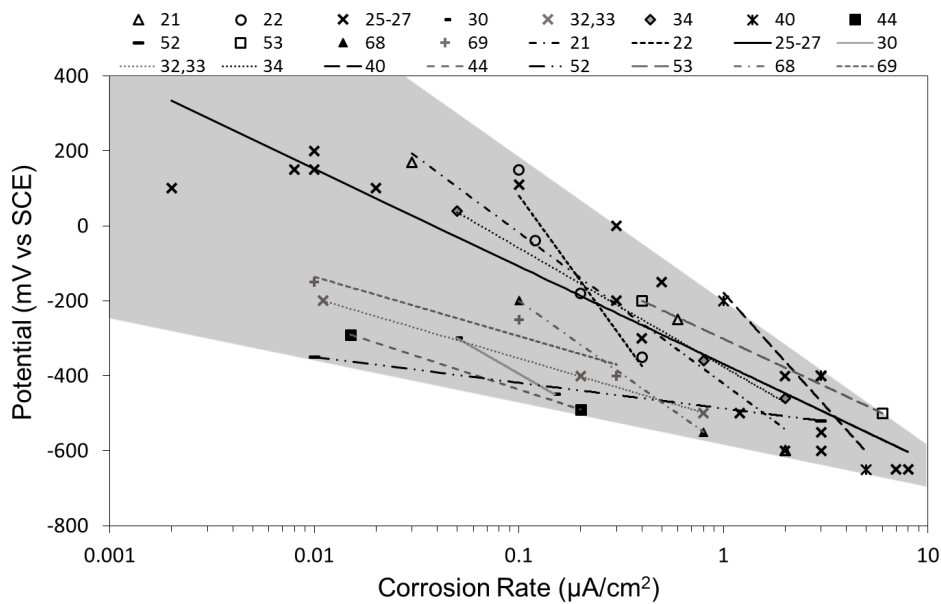
366  
367 Only few of the studies did – apart from presenting the results – analyze relationships  
368 between different parameters measured and discuss the working mechanism of corrosion in  
369 carbonated concrete or mortar. The main parameters that have been sometimes monitored  
370 but rarely evaluated and correlated with the corrosion rate are:

- 371 – Corrosion potential ( $E_{\text{corr}}$ ) of the embedded steel.
- 372 – Water presence (RH or water contact conditions).
- 373 – Resistivity ( $R_{\Omega}$ ) of the paste/mortar/concrete matrix.

374

##### 375 4.1. Correlation between corrosion potential and corrosion rate

376 33 of all the reviewed papers report the corrosion potential  $E_{\text{corr}}$  together with data on the  
377 corrosion current density  $i_{\text{corr}}$  [21, 22, 25-27, 30-35, 37, 39, 40, 43, 44, 47, 50, 52-54, 56-59,  
378 61, 63, 64, 66, 68-70, 72, 73]. An increase of the corrosion rate is generally found at more  
379 negative potentials in spite of differences in material composition, exposure condition or  
380 experimental procedure. The corrosion potentials  $E_{\text{corr}}$  span over a wide range (Fig. 6), i.e. in  
381 the papers from Alonso et al. [21, 25-27] values go from relatively high values of +200mV vs  
382 SCE in dry conditions (50% RH,  $\sim 0.01 \mu\text{A}/\text{cm}^2$ ) to -700mV vs SCE in partial immersion  
383 condition with corrosion currents in the order of 2-10  $\mu\text{A}/\text{cm}^2$ .



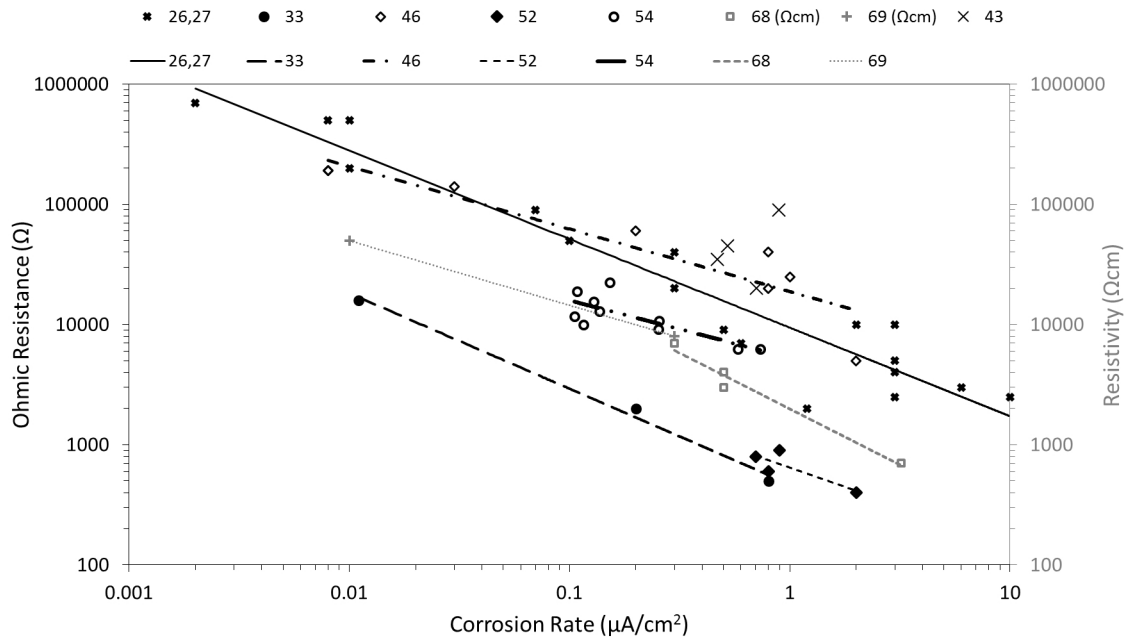
384

385 Figure 6: Compilation of the data from literature reporting the corrosion rate  $i_{\text{corr}}$  and the open  
 386 circuit potential in the OCP vs  $\log(i_{\text{corr}})$  plot.

387 The compilation of data extrapolated from the publications (Figure 6) shows a trend of  
 388 increasing corrosion rate at more negative potentials. The great variations observed in the  
 389 corrosion potential at low corrosion rate (corresponding to dry conditions) might be due to  
 390 inherent difficulties of the measurement. The data in Fig. 6 were interpreted by some authors  
 391 [21, 33] in terms of an Evans diagram, indicating the corrosion process being under anodic or  
 392 ohmic control. Glass et al. [33] present the relationship between corrosion potential and  
 393 corrosion rate (Fig. 5 in their work [33]).

#### 394 4.2 Correlation between $i_{\text{corr}}$ and $R_{\Omega}$

395 Several papers report both corrosion rate and electrical resistance of the samples [26, 27, 33,  
 396 43, 46, 52, 54, 68, 69]. The evaluation of the reported data is sometimes difficult because the  
 397 two parameters were not always plotted in the same graph [26, 27, 33]. The electrical  
 398 resistance was expressed in different ways: some authors reported resistivity measurements  
 399 ( $\Omega \cdot \text{cm}$ ) [68,69], others just an uncompensated ohmic resistance ( $\Omega$ ) [26, 27, 46, 52], few  
 400 authors reported both [33, 43, 54]. The data reported in the mentioned publications are  
 401 presented as plot  $\log(i_{\text{corr}})$  vs  $\log(R_{\Omega})$ . As a general trend  $\log(i_{\text{corr}})$  decreases linearly with an  
 402 increase in  $\log(R_{\Omega})$  of the material (Figure 7). Data from one paper [43] fall in a narrow range  
 403 of  $i_{\text{corr}} / R_{\Omega}$  and no trend line is indicated.



404

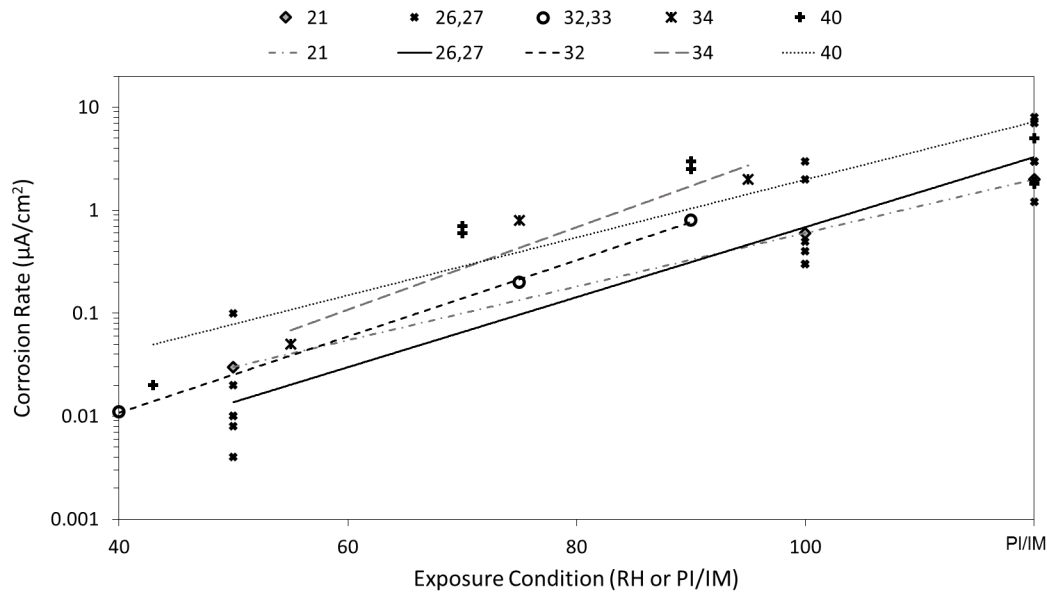
405 Figure 7: Compilation of the data from literature reporting the corrosion rate  $i_{\text{corr}}$  and the  
 406 electrical resistance or the resistivity of the material  $R_{\Omega}$  in the  $\log(i_{\text{corr}})$  vs  $\log(R_{\Omega})$  plot.

407

408 Most authors consider this correlation as proof of a direct influence of the material resistivity  
 409 on the corrosion rate (ohmic control), because the lack of matrix conductivity would inhibit the  
 410 transport of ions [26, 27, 69]. Glass et al. [33] interpreted the trend as an effect of the ohmic  
 411 resistance on the anodic reaction of the corrosion process (explained in more details below).  
 412 Other authors did not really interpret the trend between the two parameters [46,52,68]. It has  
 413 to be noted that a correlation between corrosion rate and concrete resistivity does not imply  
 414 that a mechanistic explanation exists [77].

415 4.3 Correlation between  $i_{\text{corr}}$  and water content

416 The relation between corrosion rate and water content in the pore system (represented by  
 417 means of the exposure condition and relative humidity) can be studied in 9 works [21, 26, 27,  
 418 32, 33, 34, 40, 46]. Only publications reporting corrosion rate data in more than one (defined)  
 419 exposure condition were considered for comparison, values from outdoor or indoor exposure  
 420 were not taken into account because the environmental RH was not constant. Measurements  
 421 involving the presence of chlorides were not considered, too.



422

423 Figure 8: Compilation of data showing the influence of the water content (exposure condition)  
 424 on the corrosion rate. For immersed conditions an arbitrary value of RH higher than 100%  
 425 was chosen.

426 From the data reported in Figure 8 it can be noticed that in every dataset the corrosion rate is  
 427 exponentially increasing with increasing water content. The slope of the fitted linear  
 428 correlation between  $\log(i_{\text{corr}})$  and exposure condition is quite constant among the individual  
 429 works. Individual corrosion rates at constant RH can show quite a high variability (e.g. data  
 430 from [26, 27]). This is due to the fact that the data points represent different binders and  
 431 different w/c ratios.

#### 432 4.4 Corrosion rate, ohmic resistance and water content

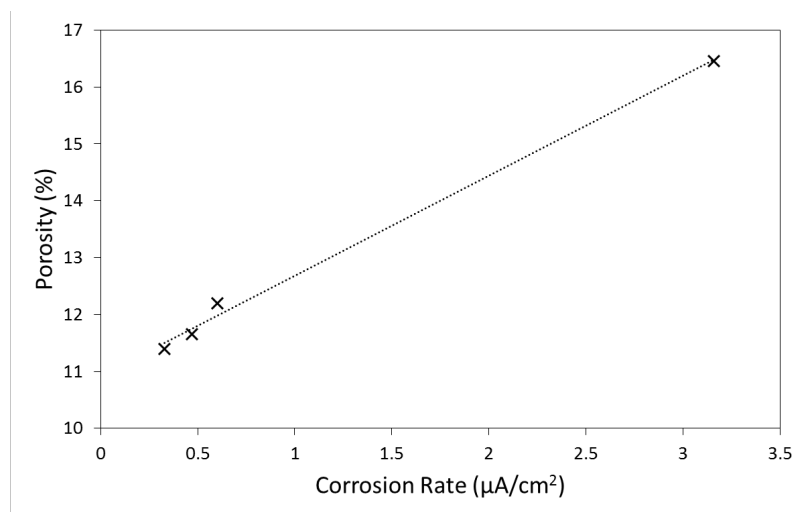
433 In conclusion it is clear that the key parameter defining the corrosion rate is the presence of  
 434 water in the pore system of the material in which the steel is embedded.

435 There are different opinions if the water content controls the corrosion process by itself or by  
 436 modifying the resistivity properties of the matrix. Some authors believe the corrosion process  
 437 to be controlled directly [26, 27] or indirectly [33] by the electrical resistance of the mortar or  
 438 concrete, the presence of water changing the conductivity of the pore system. Sometimes  
 439 the correlation (Figure 8) was not commented in a mechanistic view [44, 56] or just  
 440 considered in a practical perspective, recognizing practically relevant corrosion rates only at  
 441 RH higher than a certain value, for example 50% RH [21]. Only Dhir et al. [34], studying OPC  
 442 and fly ash binder at 55, 75 and 95% RH, interpreted the correlation (Figure 8) as direct  
 443 effect of water, stating that “the final corrosion rate was controlled by amount and  
 444 composition of electrolyte present at the steel surface” [34].

445 Based on the two previous paragraphs on correlations of corrosion rate with electrical  
446 resistance (4.2) and water presence (4.3), a similar correlation between electrical resistance  
447  $\log(R_{\Omega})$  and exposure condition can be inferred and established. When a change in material  
448 resistivity is detected as consequence of a change in the relative humidity this is associated  
449 to a change in water content in the pore system. This correlation between  $R_{\Omega}$  and water  
450 content was just taken as granted in the publications cited and was not object of mechanistic  
451 considerations.

#### 452 4.5 Corrosion rate and porosity

453 The influence of porosity on the corrosion rate has been explicitly studied only in the paper of  
454 Andrade et al. [68]. In this study the authors carried out corrosion tests in partial immersion  
455 conditions of carbonated mortar samples prepared with different binders and also reported  
456 total porosity values of those carbonated mortars measured by mercury intrusion porosimetry  
457 (MIP). As it is shown in Figure 9 a linear correlation could be found between the two  
458 parameters (although the data is scarce). Andrade et al. proposed a corrosion process  
459 controlled by water content and total porosity [68].



460

461 Figure 9: Relation between the corrosion rate and porosity in partially immersed condition  
462 [68].

#### 463 4.6 Opinions on mechanism of steel corrosion in carbonated concrete

464 Only few papers analyzed and discussed the mechanism of steel corrosion in carbonated  
465 mortar or concrete. The evolution of the opinions proposed to explain the experimental  
466 findings of corrosion of steel in carbonated concrete is shown in Table 6.

467 Several authors [25-27,30, 54, 69], based on the relation between the corrosion rate and  
468 ohmic resistance or concrete resistivity (Fig. 7) stated that corrosion of steel in carbonated  
469 mortar or concrete is controlled primarily by concrete resistivity and thus under *resistive or*

470 *ohmic control*. Glass et al. [33] pointed out that ohmic control is in contrast to the exponential  
471 relationship between corrosion rate and potential (Fig. 6), according to theory the ohmic  
472 control would lead to an almost constant corrosion potential for changing corrosion rate.

473 The inverse proportionality between  $E_{\text{corr}}$  and  $\log(i_{\text{corr}})$  (Figure 6) has been interpreted by  
474 several authors [21, 33, 58, 59] as the corrosion process being under *anodic control*. Glass  
475 et al. [33] present a detailed discussion on this point. Based on the fact that the corrosion  
476 potential becomes markedly more negative as the corrosion rate increases (Fig. 6), these  
477 authors concluded that the higher corrosion rate at more negative potentials is caused by a  
478 change in the anodic Tafel slope. Gonzalez et al. [21] discussed the mechanism of steel  
479 corrosion process in carbonated mortar on the basis of the Evans diagram (Fig. 7 in their  
480 paper [21]), taking into account that carbonation implies passivation breakdown and a  
481 parallel shift of the cathodic polarization curve to more nobler values due to the pH-drop.  
482 They conclude that it is not the oxygen diffusion to the reinforcement that controls the  
483 corrosion kinetics, but that modifications of the anodic reaction are rate determining.

484 In order to explain the pronounced dependence of the corrosion current on potential (Fig. 6)  
485 and simultaneously the strong correlation between concrete resistivity and corrosion rate (Fig.  
486 7), Glass et al. [33] proposed an improved model that takes into account both of these  
487 controlling processes and he suggested the term *anodic resistive control*. According to this  
488 concept the anodic reaction is under resistive control and the overall corrosion rate under  
489 anodic control. The corrosion process is controlled by the anodic dissolution reaction of the  
490 steel (Fig. 6) that is in turn influenced by the electrical resistivity viz. the water content in the  
491 pores controlling the dissolution and diffusion of iron ions after the oxidation reaction.

492 Some authors proposed that the anodic dissolution would be controlled by the *electrolyte*  
493 *presence at the steel/matrix interface* [34, 37] or by the total water content related to the total  
494 porosity [68] (Figure 9).

495 Table 6: Different opinions reported in the referenced works regarding mechanism of steel  
496 corrosion in carbonated concrete.

<b>Reference</b>	<b>Remarks</b>
<i>Gonzalez et al. (1980) [21]</i>	Anodic branch modifications are basically rate determining.
<i>Gonzalez et al. (1983) [22]</i>	The pH value and the concrete resistivity seem to control the corrosion rate in carbonated concrete.
<i>Alonso et al. (1987-1988) [25-27]</i>	The electrical resistivity of concrete seems to be a factor that controls the corrosion rate.
<i>Feliu et al (1989) [78]</i>	Ohmic control of the corrosion process has been shown to be incorrect.
<i>Glass et al. (1991) [33]</i>	The corrosion rate is under anodic resistive control.

<i>Dhir et al. (1992) [34]</i>	The process is controlled by amount and composition of electrolyte present at the steel surface.
<i>Lopez et al. (1993) [37]</i>	The degree of pore saturation determines the active state corrosion mechanism at the steel/concrete interface.
<i>Saguez et al. (1997) [43]</i>	Corrosion process limited by the electrolyte availability.
<i>Smith et al (2004) [54]</i>	The higher the electrical resistivity, the more difficult it is for ions to travel through the concrete, thus inhibiting corrosion.
<i>Gulikers J. (2005) [77]</i>	A linear relationship does not imply that concrete resistance is dominating the overall corrosion. / It seems very unlikely that concrete resistivity does not play a decisive role.
<i>Dangla et al. (2009) [79]</i>	The corrosion current is controlled by the transport of water rather than by the transport of charges.
<i>Andrade and Buják (2013) [68]</i>	The key controlling parameter is the volumetric water content that depends on the total porosity and its degree of saturation.
<i>Cavez-Ulloa et al. (2013) [69]</i>	When RH is reduced, $R_{\Omega}$ increases and $i_{\text{corr}}$ decreases due to an ohmic effect.
<i>Hornbostel et al. (2013) [80]</i>	The exact influence of the concrete resistivity on the corrosion process cannot be identified.

497

498

499

## 500 **5 Discussion**

501 Different mechanisms of steel corrosion in carbonated concrete have been proposed (see  
502 chapter 4.5) and the topic is still under discussion. According to the authors of this review two  
503 main difficulties have to be faced: first, important parameters monitored in addition to the  
504 electrochemical data  $E_{\text{corr}}$  and  $i_{\text{corr}}$ , mainly the resistivity of the material (or  $R_{\Omega}$ ) and the  
505 presence/amount of water, are difficult to evaluate in an independent way because a change  
506 in the water content leads to a change in the ohmic resistance / resistivity of the material.  
507 Second, the porosity (or better the pore size distribution) of the carbonated mortar or  
508 concrete samples can change with the type of binder and w/b ratio. This would influence the  
509 capillary condensation of water vapor in the pore system viz. the water content, and in turn  
510 the oxygen diffusion to the steel, the electrical resistivity and finally also the corrosion rate.

511

### 512 5.1 Influence of porosity on corrosion rate

513 Higher porosity has been found to correlate with higher corrosion rates [68], as shown in  
514 Figure 9 for a specific system. Most of the publications of this review comparing different  
515 binders found higher corrosion rates in case of clinker replacement, generally proportional to  
516 the substitution level (chapter 3.4). This tendency of low clinker cements to show higher  
517 corrosion rates in moist conditions is evident from Figure 5.

518 This trend may be explained by physical and microstructural properties of different binders in  
519 carbonated conditions. Carbonation leads to a reduction in *total* porosity [81-85] that is  
520 ascribed to the positive difference of molar volume between the calcium carbonate formed  
521 and the initial hydration products. However reducing the clinker content a shift of the capillary  
522 porosity to coarser pore size distributions was reported [85-89].

523 These shifts in the pore size distribution of the clinker reduced carbonated cementitious  
524 material to higher capillary pore size are of major importance in defining the capillary  
525 condensation of water in the concrete matrix [1] as has been discussed by Lopez and  
526 Gonzalez [37]. A higher amount of water in the pore system reduces the transport of oxygen  
527 but facilitates the dissolution and migration of ions influencing the corrosion rate. Indeed, in  
528 immersed, partially immersed or high relative humidity condition (RH > 80%) where also the  
529 capillary pores are filled, a higher porosity (due to clinker replacement) means a higher water  
530 content in the bulk of the material and presumably also on the steel surface. At low RH (<  
531 80%) the larger capillary pores are becoming empty (capillary condensation no more  
532 possible) and the amount of water in the pore system decreases. The question if the  
533 corrosion rate of steel in carbonated concrete is ohmically controlled as suggested by some



534 authors [21,33, 58, 59] or if less water is available at the steel/concrete interface for the  
535 anodic and cathodic reactions as suggested by other authors [34, 37, 68] is discussed below.

## 536 5.2 The role of water in corrosion of steel in carbonated concrete

537 The decisive importance of the environmental condition is mentioned in most of the papers  
538 dealing with reinforcement corrosion in carbonated concrete. Corrosion rate is negligible in  
539 dry indoor climate and in conditions of complete water saturation [1, 90]. The amount of  
540 water contained in the pores of mortar or concrete equilibrates with the relative humidity (and  
541 temperature) of the atmosphere. This equilibrium determines – for a given pore size  
542 distribution (see above) – the adsorption/desorption isotherms, thus the degree of saturation  
543 of the concrete pores (PS) and a number of physico-chemical properties of concrete  
544 including gas diffusion through the pores and electrical resistivity, both influencing the  
545 corrosion kinetics at the steel/concrete interface [1, 37, 90]. The condensation of water in the  
546 pore system may be described by the Kelvin-Laplace equation [91]: Each pore radius  $r$   
547 corresponds to a relative humidity at which all pores with radius  $r$  and smaller will be  
548 saturated. At increasing relative humidity the pore system gets more and more filled with  
549 water (the degree of pore saturation increases). The influence of  $w/c$  ratio and porosity on  
550 the relation between relative humidity and degree of pore saturation, sorption and desorption  
551 isotherms, may for example be found in [92]. The limit of applicability rises when it comes to  
552 saturation of large capillary pores (diameter  $>$  ca. 50-200 nm), that is expected only in  
553 contact with liquid water on the surface (immersed condition), as adsorption processes  
554 become negligible and transport processes control the system [93].

555 Electrical resistivity: The relationship between the degree of pore saturation (PS) and  
556 electrical resistivity has been studied [37, 82]. The results indicate that the electrical  
557 resistivity of concrete remains low and relatively constant in the range of 100 – 70 % pore  
558 saturation. Further decrease in the degree of pore saturation in the range from 70 – 30%  
559 corresponds to a marked increase of the electrical resistivity by two [82] or three orders of  
560 magnitude [37].

561 Oxygen diffusion: The moisture state of concrete is important for the corrosion rate due to the  
562 oxygen diffusion process. The diffusion coefficient of oxygen  $D_{O_2}$  in air (open pores) is about  
563  $10^4$  times greater than in a liquid phase (pores filled with water) [94]. When the water content  
564 viz. the degree of pore saturation is low enough to allow the formation of a *continuous path of*  
565 *open pores from the surface to the reinforcement*, termed critical pore saturation  $PS_{crit}$ , a  
566 fraction of the steel surface will be in contact with air (but still covered by a very thin film of  
567 electrolyte). The electrochemical potential of the steel surface in contact with the open pores  
568 will markedly increase compared to the potential of the steel surface in contact with liquid

569 water as has been reported by Stratmann for atmospheric corrosion of iron [95]. This was  
570 explained by the more noble iron oxides that are formed and kept, by transport limitations in  
571 the thin water film, at the steel surface and thus determine the potential. This explanation  
572 may also be applied to the observation in the literature regarding increasing potentials with  
573 decreasing moisture states, i.e. that the measured corrosion potential of steel in mortar or  
574 concrete in the range from  $PS_{crit}$  (approx. 70% - 80% RH according to [37, 90, 94]) to  
575 completely drying out increases with decreasing relative humidity.

576 *Corrosion rate:* for corrosion of the steel to take place, the presence of an electrolyte at the  
577 steel surface is necessary. Despite this statement seems trivial it is well established in  
578 atmospheric corrosion [95] that corrosion at the atmosphere is possible only above a critical  
579 relative humidity  $RH_{crit}$  when a water film is formed on the surface. The similarity with  
580 corrosion of steel in carbonated concrete has been highlighted earlier [37, 96]: when the  
581 relative humidity for atmospheric corrosion or the degree of pore saturation for steel in  
582 carbonated concrete is low enough, corrosion stops. Considering the influence of the water  
583 content in the pore system, the corrosion rate will be negligibly low when the fraction of steel  
584 surface in contact with liquid water tends to zero [90]. Contrary, the measured corrosion rate  
585  $i_{corr}$  will increase proportionally to the fraction of steel surface in contact with liquid water, thus  
586 with the degree of pore saturation [17, 37, 90, 94]. This would correspond to the hypothesis  
587 proposed in [34, 37, 68] where the corrosion rate is controlled by the amount and distribution  
588 of electrolyte at the steel/concrete interface.

589 The term "corrosion rate" and the value  $i_{corr}$  used so far have to be critically examined. As  
590 shown in Table 4, most of the corrosion rate data reported are calculated from the  
591 experimentally measured polarization resistance  $R_p$ . From the value  $R_p$  (in Ohm) the total  
592 corrosion current  $I_{corr}$  is calculated with  $I_{corr} = B/R_p$ ; referred to the geometrical area of the  
593 steel,  $A_{steel}$ , an apparent corrosion rate  $i_{corr}$  is calculated assuming homogeneous corrosion. It  
594 is this apparent corrosion rate  $i_{corr}$  that is reported in all the Figures and Tables above. In a  
595 water filled pore system the geometrical area of the steel will be equal to the effective area of  
596 the steel,  $A_{eff} = A_{steel}$ , thus the effective corrosion rate  $i_{corr,eff}$  will be equal to  $i_{corr}$ . Decreasing  
597 the relative humidity of the environment, the water content in the pore system will decrease  
598 and the steel surface in contact with water filled pores,  $A_{eff}$ , will decrease too. Thus the  
599 measured corrosion rate  $i_{corr}$  will decrease going to lower RH (Figure 8) due to this area  
600 effect, but the effective corrosion rate  $i_{corr,eff}$ , related to  $A_{eff}$ , will be the same.

601 To summarize, the impact of different exposure conditions can be seen as leading to a  
602 different extent of wet steel surface, instead of differences in the effective corrosion current  
603 density. As only the wet surface can be electrochemically active, the higher the wet surface  
604 the higher the measured corrosion rate will be.

605 5.3 Mechanistic considerations

606 With the key parameter degree of pore saturation, PS, the different empirical relations and  
607 the different parameters influencing the corrosion rate of steel in carbonated mortar can be  
608 rationalized:

- 609 • The empirical relation between resistivity and corrosion rate (Fig. 7) is found because  
610 both,  $R_{\Omega}$  and  $i_{\text{corr}}$ , are influenced (in opposite way) by the degree of pore saturation in a  
611 wide range of two or three orders of magnitude [37, 82]. Figure 7 is thus a parametric  
612 plot and does not indicate any causality – implying also that corrosion of steel in  
613 carbonated concrete is not under ohmic control.
- 614 • The empirical relation between the corrosion potential and the apparent corrosion rate  
615 of steel in carbonated mortar (Fig. 6) can be rationalized by the influence of the degree  
616 of pore saturation on the steel area in contact with water,  $A_{\text{eff}}$ . The apparent corrosion  
617 rate  $i_{\text{corr}}$  increases markedly with the degree of pore saturation [37], thus with increasing  
618 RH. The variations in the corrosion potential instead can be related to a change in the  
619 anodic behavior of the steel: in wet conditions the potential is quite negative and  
620 governed by the active dissolution  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ . In mostly dry conditions where the  
621 steel is in contact with humid air the corrosion reaction is controlled by a (porous) oxide  
622 film on the steel surface, easy access of oxygen [95] and thus much more positive  
623 potentials are measured. Strictly speaking, also Figure 6 is a parametric plot and not  
624 indicating causality.
- 625 • The exponential increase of the corrosion rate with relative humidity found for a large  
626 set of w/b ratios and binder types (Fig. 8) is reflecting the concept that corrosion rate is  
627 controlled by the amount and distribution of the electrolyte at the steel / concrete  
628 interface (see area effect above). It might be that, converting the relative humidity data  
629 for each system studied to a degree of pore saturation (requires knowledge of the  
630 adsorption isotherm), the scatter in Fig. 8 might be reduced.
- 631 • The proportionality between corrosion rate and porosity observed (Fig. 9) reflects the  
632 fact that – at a given degree of pore saturation – a higher porosity leads to a higher  
633 steel surface in contact with water,  $A_{\text{eff}}$ , and thus, due to this area effect, to a higher  
634 measured corrosion rate  $i_{\text{corr}}$ .

635 The concept presented based on the degree of pore saturation, thus the presence of water  
636 on the steel surface, providing an electrolyte for the anodic and cathodic electrochemical  
637 reactions, can be refined further. Permanent saturated conditions with PS 100 % should  
638 result in very low corrosion rates due to lack of oxygen supply. In conditions of wet/dry cycles  
639 the presence of rust, more specifically  $\text{Fe}^{3+}$  ions, should be taken into consideration as

640 additional cathodic reaction [95, 97-99]. Also, the pore solution composition, especially the  
641 pH, might be different using different cement blends and might influence the corrosion rate  
642 [100].

643

## 644 **6. Research needs identified**

645 As shown in this review, literature data regarding the corrosion rate of steel in carbonated  
646 concrete are scarce and refer mainly to Portland cement. As in the future more different  
647 supplementary cementitious materials (SCM) at increasingly higher replacement ratios will  
648 be used, the influence of the clinker substitution should be studied *systematically* at different  
649 exposure conditions. The following research topics have thus been identified:

### 650 6.1 Systematic data collection

651 Corrosion rate data of many different binders, w/b ratios at different exposure conditions  
652 have to be obtained in a short time. To obtain this, a new experimental set up has been  
653 designed [101]. The new test setup consists of small (8 x 8 cm) and thin (6 mm) cement  
654 mortar samples allowing rapid full carbonation (max 1 week in 4% CO<sub>2</sub>) and rapid  
655 equilibration of environmental humidity (checked by the sample weight). The samples are  
656 instrumented with a reference electrode, 5 steel wire electrodes and a stainless steel grid  
657 counter electrode. Parameters that can be measured are electrical resistivity of the mortar,  
658 corrosion potential and corrosion rate (LPR measurements) of the steel wires, oxygen  
659 diffusion and consumption rate [101].

660 The proposed test setup can minimize the time to carbonation and moisture equilibration in  
661 different exposure conditions. It is also possible to evaluate the electrochemical activity of the  
662 system without interference of moisture gradients that would almost always be present in  
663 large samples. Only in this way the system can be characterized in each exposure condition.  
664 Another advantage is that all the electrodes are already embedded, minimizing diffusion  
665 potentials between reference and working electrode and avoiding problems deriving from  
666 using an external reference electrode, such as the use of wet sponges for the electrical  
667 contact.

### 668 6.2 Mechanism of steel corrosion in carbonated concrete

669 A more complete set of data will allow studying the mechanism of steel corrosion in  
670 carbonated concrete made of different blended cements. Of particular interest are data that  
671 link the corrosion rate of steel in carbonated concrete at different RH to the porosity of the  
672 material, where only few data exist (Fig. 9), and to the steel-concrete interface [102]. The  
673 similarity of corrosion in carbonated concrete with atmospheric corrosion [96] deserves

674 further attention, especially when rust layers have already formed on the steel surface. Fe<sup>3+</sup>  
675 ions in the rust products can act as cathodic reaction driving the corrosion of steel also in  
676 situations with low oxygen content (wet/dry cycles) [95, 97-99]. Also studies in simulated  
677 pore solution could help clarify the influence of certain parameters on the steel corrosion rate,  
678 such as pore solution pH and resistivity.

### 679 6.3 Sustainable clinker replacement

680 Achieving sustainable reinforced concrete structures clearly not only requires decreasing the  
681 environmental footprint of the materials at the time of their production (reducing the CO<sub>2</sub>  
682 emission and thus the clinker content), but to combine this with high durability, thus long and  
683 maintenance free service lives of the structures in their actual exposure environments. As the  
684 carbonation rate is faster compared to OPC, the corrosion propagation stage might become  
685 a significant part of the total service life. The most critical situations for reinforced concrete  
686 structures might be long periods of relative humidity in the range of maximum carbonation  
687 rate with periodic wetting of the surface inducing high corrosion rates of the steel in  
688 carbonated concrete. Thus for the use of clinker-reduced cements no general rules can be  
689 given but the specific exposure conditions have to be taken into account.

690

## 691 7. Conclusions

692 From the present literature review the following major conclusions are drawn:

- 693 1. The corrosion rate of steel in carbonated concrete becomes (again) of great interest.
- 694 2. Literature data show that the corrosion rate generally increases with increasing clinker  
695 substitution.
- 696 3. The main parameter controlling the corrosion rate of steel in carbonated concrete is the  
697 exposure condition: at low RH the corrosion rate is negligible, significant values are  
698 reported only in very humid conditions and in direct contact with water.
- 699 4. The frequently mentioned inverse relation between concrete resistivity and corrosion  
700 rate is an empirical correlation, both parameters depend (inversely) on the degree of  
701 pore saturation of the concrete.
- 702 5. Consultant engineers should be aware that the propagation phase of corrosion can  
703 become an important part of the total service life of a structure, thus blended cements  
704 have to be applied carefully, and taking into account the exposure condition (moisture).
- 705 6. More research is needed regarding the importance of the influence of porosity,  
706 especially changes of the pore size distribution due to carbonation. Due to the huge  
707 number of different (new) binders that have to be studied in different exposure  
708 conditions the test duration should not be too long. Small, instrumented samples that

709 allow rapid full carbonation, fast equilibration to changing exposure conditions and  
710 reliable corrosion rate measurements have been proposed.

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745 **Figure captions**

746 Figure 1: Cumulative probability distribution of the minimum and maximum corrosion rate  
747 reported in literature (see Table 1).

748 Figure 2: Compilation of the reported minimum and maximum corrosion rate values of steel  
749 in carbonated mortar or concrete in different exposure conditions (RH) corresponding to  
750 XC3. For each literature reference the w/b ratio(s) and the binder(s) studied are indicated.

751 Figure 3: Compilation of the minimum and maximum corrosion rate of steel in carbonated  
752 mortar or concrete in exposure conditions that imply contact with liquid water (XC4). For  
753 each literature reference the w/b ratio(s) and the binder(s) studied are indicated.

754 Figure 4: Summary of corrosion rate data from literature works studying the influence of  
755 different exposure conditions (immersed, constant RH, outdoor and indoor). For each  
756 literature reference the w/b ratio(s) and the binder(s) studied are indicated.

757 Figure 5: Reported corrosion rate values (interval min – max) of steel in carbonated mortar or  
758 concrete made with different binders exposed to different environments.

759 Figure 6: Compilation of the data from literature reporting the corrosion rate  $i_{\text{corr}}$  and the open  
760 circuit potential in the OCP vs  $\log(i_{\text{corr}})$  plot.

761 Figure 7: Compilation of the data from literature reporting the corrosion rate  $i_{\text{corr}}$  and the  
762 electrical resistance of the material  $R_{\Omega}$  in the  $\log(i_{\text{corr}})$  vs  $\log(R_{\Omega})$  plot.

763 Figure 8: Compilation of data showing the influence of the water content (exposure condition)  
764 on the corrosion rate. For immersed conditions an arbitrary value of RH higher than 100%  
765 was chosen.

766 Figure 9: Relation between the corrosion rate and porosity in partially immersed condition  
767 [68].

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