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Reinforcement corrosion initiation and activation times in concrete structures exposed to severe marine environments

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ABSTRACT

The corrosion of steel reinforcement bars in reinforced concrete structures exposed to severe marine environments usually is attributed to the aggressive nature of chloride ions. In some cases in practice corrosion has been observed to commence already within a few years of exposure even with considerable concrete cover to the reinforcement and apparently high quality concretes. However, there are a number of other cases in practice for which corrosion initiation took much longer, even in cases with quite modest concrete cover and modest concrete quality. Many of these structures show satisfactory long-term structural performance, despite having high levels of localized chloride concentrations at the reinforcement. This disparity was noted already more than 50 years ago, but appears still not fully explained. This paper presents a systematic overview of cases reported in the engineering and corrosion literature and considers possible reasons for these differences. Consistent with observations by others, the data show that concretes made from blast furnace cements have better corrosion durability properties. The data also strongly suggest that concretes made with limestone or non-reactive dolomite aggregates or sufficiently high levels of other forms of calcium carbonates have favourable reinforcement corrosion properties. Both corrosion initiation and the onset of significant damage are delayed. Some possible reasons for this are explored briefly.

1. Introduction

The early occurrence and high rate of corrosion of reinforcement in concrete structures exposed to marine environments or to repeated applications of de-icing salts is a problem that has been of interest for many decades [1–3]. That the problem is still not resolved is evident in the search for remediation measures, in the uncertainty in the criteria and guidelines for the durability design of reinforced concrete structures and in the continued exploration of alternative measures and materials [4]. However, specialist treatments and new materials may not be the key to the problem since already some 50 years ago Wakeman et al. [2] posed the question 'Why do some concrete structures seem to last indefinitely in seawater while others deteriorate within a comparatively short time?' Similarly, some 30 years later, Burkowsky and Englot [5] note that for New York and New Jersey road bridges a wide variation in durability performance was observed, even for major bridges that are essentially similar in design and construction. While some have required extensive maintenance, others are '… standing up well — even after 60 years of service. Why the difference?'

Wakeman et al. [2] proposed some answers that have been echoed many times since, based both on experience and on research. They advocated 'dense, impervious, relatively nonabsorbent concrete', a minimum concrete cover of 3 in. (75 mm), sufficiently high cement content, a low water/cement ratio, non-reactive aggregates and good compaction and curing. These are consistent with what currently is still considered good practice. These desiderata are based on the accepted notion that in marine environments chloride ions are aggressive to the passive layer assumed to exist on the exterior of steel reinforcement and that breakdown of this layer causes localized corrosion [6–8]. However, there are structures in practice exposed to extremely aggressive marine environments for which one or more of the desiderata have been violated, yet the structures have lasted many years with little or no signs of corrosion. For example, Burkowsky and Englot [5] commenting on the effectiveness of conventional predictive tools, such as polarization resistance and pH measurements and chloride concentrations noted that typically '…test results for the good decks (that) could not be separated easily from those for the problem decks…' and '…so-called "indicator tests" were contradicted by… actual deck performance.' They found that very high chloride contents, in excess of 1 lb per cu. yd of concrete (approx 0.2% by cement), were common without a corresponding history of reinforcement corrosion. Similarly, Borgard et al. [9] note the occurrence of high levels of chloride adjacent to reinforcement that has not corroded

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and reinforcing steel 'removed from concrete after many years with no indication that it has ever been exposed to a wet environment'.

One of the difficulties with these various comparisons is that usually different structures of different complexities at different locations with different micro-climates and built to differing design and construction standards are being compared. Moreover, there usually are also differences in detail design and considerable variability in construction and workmanship practices. Usually these factors taken together make comparison of the performance of reinforced concrete structures problematic. However, this is not always the case.

Recently, Melchers and Li [10] reported the very considerable difference in durability performance of some 1000 very simple and almost identical reinforced concrete elements all exposed to the same aggressive marine environment of the North Sea at Arbroath, Scotland. This means that differences due to location and micro-climate and in structural form and hence exposure are negligible and that only differences in materials are of interest. It is therefore noteworthy that over 90% of the elements constructed in 1943 had survived to 2006 with almost no evidence of corrosion initiation despite their being of apparent lower quality concrete than subsequent elements. These were constructed in 1968 and 1993 and show severe reinforcement corrosion and longitudinal cracking of the elements. Tests showed that concrete permeability for the three concretes was generally similar and chloride concentrations at the reinforcement was as high for the 1943 elements as for the 1993 elements but much higher than that for the badly corroded 1968 elements. While only limited pH readings could be taken on the few cross-sections available to the investigators, they did not suggest much difference in concrete alkalinity between the three concretes even though the concretes are of very different ages. Detailed examination showed that unlike the subsequent elements, the 1943 elements were all constructed with seashells in the concrete mix. Seashells are predominantly aragonite, one of the polymorphs of calcium carbonate. Because construction records are no longer available, it is uncertain whether the seashells were rinsed with fresh water prior to use and whether seawater was used in the 1943 concrete.

The aim of the present paper is to investigate whether there are other cases reported in the literature for which there is correlation between reinforcement durability, elevated levels of calcium carbonate in the concrete matrix and concentration of chlorides at the level of the reinforcement. Of particular interest are observations and data for actual reinforced concrete structures under marine exposure conditions or subject to de-icing salts. Unfortunately, and for obvious reasons, there are almost no systematic observations directly of reinforcement bars in actual structures and how that reinforcement corrodes as a function of exposure time for realistic exposure conditions. Mostly what is available are data for observations of the external surfaces of concrete structures. Such observations are used herein, using data extracted from the open literature, both for in-situ observations and for some laboratory tests.

2. Background

Corrosion of reinforcement usually is considered to initiate when chlorides from the external environment have penetrated sufficiently far into the concrete matrix to reach the reinforcement in concentrations high enough to break down the passive layer on surface of the reinforcement [6]. Such chlorides can arise from seawater or salt-spray particles. Chlorides also may originate from de-icing salts where these are used on road bridges.

One role for the concrete surrounding the reinforcement is to provide physical protection against the migration of aggressive chloride ions. The other role of the concrete is that it provides an alkaline environment around the bars. The alkalinity of the concrete soon after casting typically is high and this develops a passive layer on the surface of the reinforcement. For mild and low alloy reinforcing steels this usually inhibits the initiation of the corrosion process. The high alkalinity is the result of the presence of highly alkaline calcium, sodium and potassium hydroxide ions. It has been observed, however, that the hydroxide ions can leach out of the concrete slowly with time [11–14]. Perhaps in combination with concrete carbonation, this will contribute to the gradual lowering of the alkalinity surrounding the reinforcement bars and the observed lower pH value of older concretes. Eventually this leads to the initiation of corrosion of the reinforcement.

There are numerous observations that corrosion initiates at voids, air pockets or pores in the concrete immediately adjacent to the reinforcement, that is, at locations where there is no immediate presence of alkalies [15,16] and there is a small local pocket or limited supply of oxygen. As a result, initial corrosion typically occurs as localized corrosion (sometimes called pitting corrosion).

While the process of corrosion initiation is controlled by the pH of the concrete and hence by the availability of a sufficiently high level of hydroxides, influenced in marine conditions by the presence of aggressive chloride ions, the process of subsequent continued corrosion is through oxidation of the reinforcement. As for bare steel in the atmosphere and under immersion conditions, the rate of oxidation is controlled primarily by the rate of supply of oxygen to the reinforcement impeded by the concrete cover [17,18].

It is conventional in many practical applications to use a simplified model to represent the changing pattern of corrosion loss with time. The most common approach does not deal directly with the corrosion of the reinforcing steel at all, but with its consequences, such as cracking, spalling and rust staining of the concrete, measured through the index 'damage' [19,20] even though this is obviously a parameter that can be defined only imprecisely. The usual assumption is that zero damage (and by implication insignificant corrosion) occurs prior to the reaching of some threshold time t_t sometimes known as the 'corrosion initiation time' (Fig. 1a). Since the relationship in Fig. 1a is in terms of damage, a more correct interpretation of t_t in this context is that it indicates the commencement of damage and in turn that this means the commencement of significant corrosion. In this model damage usually is assumed to increases linearly with time after t_t. This model is the well-known bi-linear 'damage' model. It has a considerable history and is widely advocated [8,21].

In applications of the bi-linear damage model it is customary (and conservative) to assume that the cessation of adequate structural performance occurs at the onset of significant damage, that is, at time t_t (Fig. 1a). This threshold of unacceptable damage is linked to a threshold chloride level, or, in other treatments, to a threshold ratio of the concentrations of chlorides to hydroxides at the reinforcement. The implication is that low levels of chlorides would not initiate corrosion. However, there have been many reports of reinforcement corrosion having initiated much earlier, as evident by rust stains and minor surface cracking sometimes with rust stains but with little or no evidence of further corrosion until much later (e.g. [24]). For this reason it is appropriate to add an earlier threshold, that of corrosion initiation, at time t_i and to distinguish this from active corrosion that occurs at a subsequent time t_{ac} (Fig. 1b) [22, 23].

Because of the importance conventionally attached to chlorides in the corrosion of reinforcement there has been much research attempting to define the threshold limit below which the action of chloride ions is considered to be of little importance [6,8]. Attention has been given also to the role of bound chlorides and much less attention to the leaching of hydroxide ions. Most research effort has been devoted to understanding the transportation of chlorides from the external environment into the concrete towards the reinforcement, often simplified by assuming Fickian (i.e. so-called 'linear') diffusion controls the process, whereas the reality is more complex. This has led to adaptations of the simple theory to meet field observations, with the diffusivity described by an equivalent system with an 'apparent' diffusivity coefficient [7]. Despite these extensive

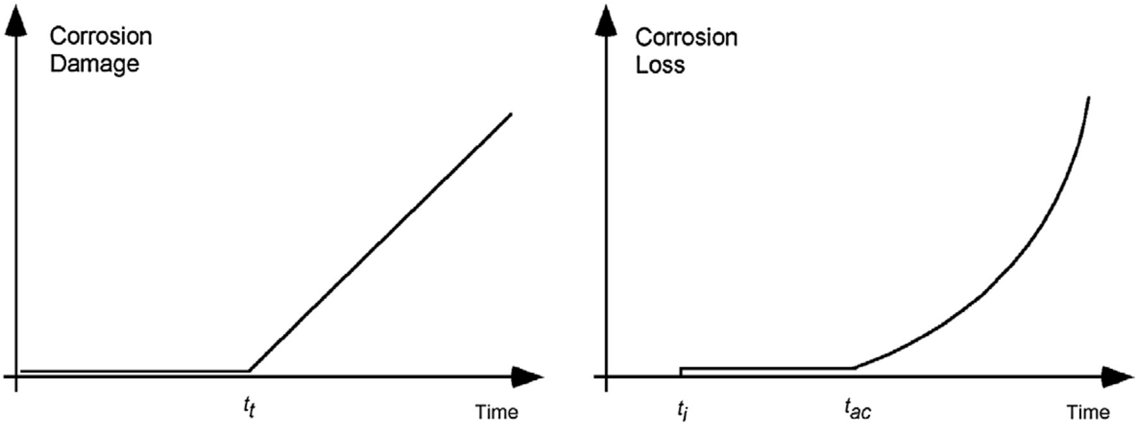

Fig. 1. (a) Bi-linear 'damage' model showing the threshold time t_t prior to which no damage is assumed to occur and subsequent to which linear damage accumulation is assumed, and (b) more sophisticated model in terms of corrosion of the reinforcement showing the time t_i at which corrosion initiation occurs and the time t_{ac} at which long-term corrosion is activated [22,23].

efforts, both the critical chloride (or the chloride/hydroxide) threshold level and the transportation mechanisms are still not well defined or understood [16].

As noted, there are actual field observations reported in the literature that suggest that very considerable levels of chloride can be tolerated at the reinforcement without apparent occurrence of corrosion initiation and hence with little or no obvious adverse structural or serviceability consequences (e.g. [5,10,25,26]. Mostly these observations have been ignored in the development of theories for the initiation (and to a lesser extent the progression) of reinforcement corrosion. The following provides a summary of several examples described in the literature.

3. Observations

Table 1 summarizes cases extracted from the corrosion and engineering literature for which sufficient information was available (or could be deduced) about the initiation and/or the progression with time of reinforcement corrosion. Table 1 shows the reported chloride concentrations at the reinforcement, converted where possible to percentages of cement content. In some cases estimates of the chloride content were made. Table 1 also shows information about cement type and about aggregates where this was available or could be reasonably deduced.

Two indicators of durability were extracted or estimated from the reported information for each case. The first is the time from first exposure to when rusting of the reinforcing bars commences, that is the 'initiation' time t_i. The second is the time t_{ac} from first exposure to active reinforcement corrosion, estimated as occurring at about the time significant damage such as cracking and spalling was observed. Where the data had to be interpreted to provide estimates of chloride content, t_i or t_{ac} the figures in Table 1 are shown in square brackets.

Wiebenga [27] and Bijen [28] both report the excellent performance of coastal structures in the Netherlands, many constructed using blast furnace slag cement. Concretes made with this type of cement have been noted to show better durability properties in marine environments than do concretes made using normal cements (and without additives such as fly-ash). In-situ chloride measurements showed low chloride concentrations next to the reinforcement. This was attributed to the blast furnace slag cement producing a less permeable concrete. Laboratory observations support this conclusion [29]. The initiation times for these data have been estimated since there is little in the documentation to provide firm information. Lea and Watkins [30] report on the effect of blast furnace cements as well as OPC and other cements on cracking due to reinforcement corrosion in experimental piles but provide little other information, including on chloride concentrations.

The papers by Cavalier and Vassie [31,32] mention the cases shown in Table 1 although again details of initiation time and longer-term behaviour are scanty. Importantly, all these structures showed corrosion within 18 years after construction, even though they were constructed in the mid-to-late 1950s. This means that changes in the making of OPC (ordinary Portland cement) [33] are unlikely to be directly responsible for what is sometimes claimed to be the poorer durability performance of concrete made using modern cements [34].

The reinforcement corrosion performance of various Norwegian coastal structures is described by Gjorv [35] and Gjorv and Kashino [36]. Details such as cover are not given and only indicative information is provided about chloride concentrations. Gjorv and Kashino [36] observed that the rate of chloride diffusion for the Oslo Harbor piling was only about half that observed after 40 years of exposure for the piling of the old San Mateo-Hayward Bridge in the USA [37] and suggests that this is a result of 'a difference in concrete quality between the two structures'. The Oslo Harbor pier was subject to severe frost damage and this led to several repair phases. However, most of these did not appear to be related to damage caused by reinforcement corrosion, despite the original concrete in the structure being rated, after demolition, as of 'low quality and…not air entrained' [36]. As dolomites are quarried extensively in Norway for construction purposes, it is reasonable to assume that the concretes all contained dolomite aggregates.

Lukas [25] was one of the first to note that heavy use of de-icing salts and hence high levels of chlorides could be tolerated in road bridges without apparent ill-effect and with corrosion of the reinforcement only rarely being detected. The bridges were located in Austria and, although not mentioned, it is likely that the Austrian aggregates were (non-reactive) dolomites. Lukas also notes that some earlier UK road bridges showed no evidence of reinforcement corrosion despite the use of de-icing salts. This may be contrasted with other UK bridges [38] that showed significant reinforcement corrosion problems within a few years of construction.

Cramer et al. [4] report on the severity of the reinforcement corrosion problem in the US and give examples of two road bridges in Oregon on the west coast of the US. These were demolished after about 40 years of service during which extensive maintenance was required. The failure of a variety of preventative and corrosion inhibition measures was noted. The authors do not report details of the concrete mix design, the cement type or the aggregate used. US Geological Survey information shows that aggregate sources in Oregon are predominantly 'traprock', a local name for what is an igneous rock.

Lambert et al. [39] measured corrosion currents for laboratory slab tests specimens exposed to static seawater. After an initial period of about 2 weeks of active corrosion, the corrosion current dropped to very low values and only later increased again. This is consistent with the model of Fig. 1(b). The increase in corrosion current generally was delayed for greater concrete cover and was found to depend on the ratio of wet time to dry time. Both are as expected. However, the authors did not comment on the result in the paper that showed specimens with limestone aggregate having initiation times significantly longer than those for specimens with quartzite aggregate. The same cement (OPC) was used throughout.

The data reported by Polder and Hug [40] for the corrosion of reinforcement of a footbridge requires some interpretation. The greatest deterioration occurred for a part of the bridge initially protected with an epoxy coating but when this became permeable it also retained moisture inside the concrete, thereby artificially increasing the 'time of wetness' to much higher levels than for the adjacent parapets. However, these were subjected to much lower levels of application of de-icing salts. The frequency of de-icing salt application was considered to be modest given the relatively mild winters in The Netherlands. The net result is that the time to active corrosion is over-estimated for the parapets compared with that for the epoxy-coated part of the bridge once the coating lost its protective cover, estimated as between 10 and 15 years.

Castel et al. [41,42] found no correlation between longer-term corrosion and chloride content for reinforced concrete beams exposed for 17 years in the laboratory to a saline fog environment. Although the chloride content was well above the usual thresholds there was little evidence of reinforcement corrosion. It was suggested that corrosion occurred only where there was a lack of intimate contact between the reinforcement and the surrounding concrete. This accords with the recognized notion that air pockets at the interface layer are correlated with local corrosion [15].

For the Hathaway Bridge located in coastal southern Florida, Lau et al. [26] noted that even after 42 years in-service the 76 support piles showed little sign of corrosion initiation. Exposure of the reinforcing bars revealed only a dull to lustrous grey mill scale but no discernable rust. Similarly, for the Pensacola Bridge, there was only minor corrosion after 43 years exposure. Fewer than 2% of the 908 bridge piles examined showed rust stains greater than 100 cm^2. Smaller rust stains were noted on about 25% of the piles. The Brooks Bridge, only slightly younger at 39 years, showed only some superficial rust staining. The initiation times shown in Table 1 were estimated conservatively using the published information. In view of the predominant limestone geology of southern Florida, it is likely that the aggregate noted as 'river rock' is limestone or dolomite.

Sagues [43] also dealt with bridges in Florida. These ranged in age from 18 to about 30 years and were exposed to aggressive marine conditions. In general, polarization resistance measurements indicated negligible corrosion, consistent with visual observations of low incidence of reinforcement corrosion and rust staining. This was the case also for the Florida Keys bridges that were noted as having substantial deviations from the nominal cover. It was not uncommon for the cover to be 'as little as 25 mm' and 'some instances of no cover were encountered'. The first concrete spalls were noted after only 6–9 years in-service. Since these are likely to be associated with low cover, they are not typical and the initiation time for areas of the bridges complying with design cover requirements is likely to be significantly longer.

Pronounced differences in reinforcement durability for road bridges subject to de-icing salts in New York and New Jersey led to detailed field and laboratory investigations of five selected bridges [5]. These were very similar in many critical design aspects. Details relevant to the present paper are given in Table 1. Reference to US Geological Survey reports shows that historically around 75–85% of crushed stone used for construction purposes in Pennsylvania State and New York State is limestone and dolomite. Overall aggregate production in the other neighbouring states was much lower and was predominantly igneous rock. Thus, although the source of aggregate used in each bridge cannot now be established from the available published information, it is likely that limestone or dolomite or both were used as concrete aggregate for most of the bridges.

Melchers and Li [10] observed that over 90% of simple pre-cast reinforced concrete handrails constructed at Arbroath, Scotland, in 1943 showed little or no sign of corrosion initiation even after more than 63 years of exposure to the North Sea. Some handrails were replaced in 1968 and others in 1993 for reasons that cannot now be traced, although it may be assumed that they showed signs of reinforcement corrosion. When inspected in 2003 the majority of the 1968 and 1993 replacements were found to be badly cracked longitudinally as a result of significant reinforcement corrosion. The 1943 handrails all contain seashells as part of the concrete mix. Both the 1968 and the 1993 concretes contain only igneous aggregates. Visual inspection of the interior and of exterior surfaces and concrete permeability measurements indicated that the later concretes were generally of better quality than the 1943 concrete, consistent with the war-time construction of the 1943 concrete and the obvious presence of seashells in the concrete, suggesting also the possible use of seawater for concrete mixing water. While not conclusive, these indicators suggest that if anything the 1943 concrete should have been worse rather than better than the later concretes.

4. Analysis

Table 1 shows estimates for t_i and t_{ac}. Where possible information reported in the literature is given, in other cases the Authors interpreted the available information. This is shown with square brackets.

Parameters t_i and t_{ac} are plotted in Figs. 2 and 3 respectively as a function of the reported or interpreted chloride content at the reinforcing bars. These figures require some interpretation because they have been plotted to represent the significant level of uncertainty in much of the available information. As noted above, largely this is due to its scant reporting in the original sources. For this reason all information is represented by the *range* of the information available, represented by a rounded or open rectangle. In both figures the dark grey shaded rectangles denote concretes made with blast furnace slag cements. The light grey rectangles with black borders denote concretes made with (non-reactive) dolomite or limestone aggregates or both or with seashells. The white, open rectangles with grey borders represent the remaining cases.

For each rectangle the upper and lower edges denote the range in initiation or active corrosion time. In each case the lower edge is a conservative estimate for the value reported in the literature, usually corresponding to the length of the observation period since first construction. In Fig. 3 where the upper edge is not shown an arrow indicates that the upper boundary is undefined, i.e. there is continuing good performance and little or no evidence of active corrosion. The left and right edges denote the estimated range in chloride content. Evidently a large bounded rectangle denotes greater overall uncertainty compared with a smaller rectangle. Size is not, in this case, a measure of importance but rather a measure of uncertainty. Also shown is a typical nominal chloride threshold for corrosion damage, taken here as 0.6% by weight of cement.

Fig. 2 shows that the time to corrosion initiation for ordinary concretes in many cases is quite short – within the first 5 years or so of exposure irrespective of the precise chloride content around the reinforcing bars, although for low levels of chlorides the initiation time appears to be generally somewhat longer – perhaps up to about 10 years. However, for the concretes containing limestone or (non-reactive) dolomite aggregate (or seashells (W1)) or blast furnace cement (A1 and A2), the times to initiation of corrosion are longer, and in some cases very much longer. Again lower levels of chlorides around the reinforcement appear to extend the time to initiation.

Table 1
Observed or estimated values for t_i. and t_{ac} for various cases of long-term reinforcement corrosion reported in the literature.

Code	Ref.	Structure	Age (years)	Cover (mm)	Total chloride concentration (by weight of cement)	Initiation Time (years)	Time to active corrosion (years)	Cement/concrete/aggregate	Comments
A1	[27]	Coastal structures (NL)	16-49	Varies 50 typical	Generally less than threshold.	[<20]	[>30]	Many blast furnace slag cements.	88% of 64 structures showed no corrosion. No visible corrosion if <30 years old. "No correlation with cement content."
A2	[28]	Coastal structures (NL)	30+	50 (25-75)	~0.14%	[20-25]	>30	Ditto	
A3	[1]	Coastal structures (South Africa)				≪4	<4	Granites, gneiss aggregates	
A4	[30]	Sheerness (UK) (1929) Experimental tidal piles (144)	10	25 50	?	<2 ~6		OPC, Rapid hardening	First occurrence of cracking
				25 50	?	~8 >10		Blast furnace PC	High alumina cements >10 years
B1	[31]	Haddiscoe Bridge deck (UK) (1960)	18	25	0.9%	[<15]	<18	OPC	De-icing salts Localized pitting corrosion
B2	[32]	Bridge over Great Ouse River (UK) (1964)	18	38 specified, 25 and less	0.8%	[<15]	<18	OPC	De-icing salts Localized pitting corrosion
B3	[33]	Jetty at Hout Bay (ZA) (1968)	14			[<10]	<14		Marine splash zone Localized pitting corrosion
C1	[35]	Harbour structures (219) (N) - immersed	50-60		[high ?]	<5	[~50-60]	Dolomites aggregates likely	Little corrosion evident
C2		- tidal zone			[high ?]		[~30-40]		Approx <20% steel loss
C3		- splash			[high ?]		[~30-40]		Beams corroded more than slabs
C4	[35]	Coastal Bridges (320) (N) pre 1970	>24	Varies 50 typical	High		<25	Dolomites aggregates likely	Approx 25% have 'serious' corrosion
C5		post 1970	<24			≪10	~10		Lower cement content
C6	[35]	Offshore structures (several) (N)	approx 10 years		High	≪10		Dolomites aggregates likely	'very good' condition (implies some evidence of rusting)
D1	[36]	Pier (Oslo Harbor) (N) (~1922)	60	<30	0.35-0.7%	20	[<54]	Dolomites aggregates likely	Overall 'very good condition'<25% of reinforcement corroded, <10% steel loss.
D2		demolished 1982		<50	1.0-1.8%	10	[<54]		
D3		- deck		25-50	1.5-1.8%	<14	[<60]		Extensive spalling by 1976 (54 years)
D4		- deck beams - tidal - immersion		50-120**	2.2-2.5%		[<60]		Several repairs, invariably not effective Pitting <1mm, surface cracking Pitting <0.2 mm, some 0.5 mm, little rust staining
E1	[37]	Road Bridge piles (USA)	37	45 - 55	0.8 - 1%	<1	≪37		No evidence of reinforcement corrosion for some high chloride levels.
E2	[25]	Road bridges (Austria)	20	25 - 30	>1.8%	>20	>20	Dolomite aggregates	Corrosion rarely detected even in high chloride regions.
	[5]	Road bridges (New York)							
E3		Goethals Bridge (1928)	60	50 +	0.36	<54	>60	Limestones and dolomite aggregates likely	Overall repairs mainly to asphalt
E4		GB Parallel (1964)	24	40	0.95	<18	>24		Ditto plus minor patching in 1982
E5		G. Washington HR1 (1959)	29	55	1.3	<17	>29		Ditto plus minor patching in 1976
E6		G. Washington PIP (1953)	35	62	0.6	<35	>35		Almost no patching required
E7		Outerbridge Crossing (1922)	60	25 (6-125)	>0.3	[<10]	[<20]		Low-level maintenance throughout
E8	[4]	Rocky Pt viaduct (1954)	40	28 - 67	~2.2	≪13	<15		
E9		Brush Creek Bridge (1954) Oregon (USA)	44	25 - 100	~1.1	~4	7-14		

F	[49]	Test specimens, tidal and marine spray cycles at Aberdeen Beach (UK)		0 upward	$\gg$ threshold ($[Cl^-]/[OH^-]$ 320 $\gg$ 0.61)	>3.3			Randomly distributed steel fibres in concrete. Extensive corrosion only of very outside fibre segments after 3 months (i.e. zero cover)
G1	[50]	Prisms (UK) atmosphere	10	10 & 20	?	1-2			t_i measured by first appearance of pitting on
G2		high strength rusty steel		10		1-2			reinforcement surface. CaCl added to mixes.
G3		ditto - grit-blasted		20		2-3			
		ditto - grit-blasted							
H	[39]	Test specimens (slabs)		10 → 40	$\gg$ threshold ($[Cl^-]/[OH^-]$ 3-20 $\gg$ 0.61)	~1 → 2			Artificial salt exposure conditions.
I	[51]	Jetty piles (Singapore) splash zone	24	70	~1.4%	[5-10]	[~20]	OPC	Rust stains, cracks, delamination ~30%
J	[52]	Test specimens Tokyo Bay	5	25		$\ll$5			
K	[20]	Sample beams from bridge decks - undefined locations (USA).	40 ?	27.2 47.5 69.5		<0.72 <1.84 <3.54			Beam # 18512.0 # 2859.6 # 3859.6
L	[53]	Bridge piles (tidal) (MX)	15	?	0.4-2.9%	<5	[>15]	[Limestone] aggregates likely]	
M	[54]	Test specimens (MX)	2	32	~1.2-3.6%	0.5-0.8			
N	[55]	Long Key Bridge (FL) piles (1980)	17	100	~0.4-2.4%	<6	[>17]	[Limestone aggregates likely]	Epoxy coated reinforcement
O	[56]	Laboratory specimens Range of salinities		20	<0.05 - 2.5%	<4	[~10]		Irrespective of chloride levels (including zero) obtained ‘unacceptable average corrosion rates’
P	[57]	Test beams under load		25	~1.5%	1-1.5			Averages from a number of tests
Q1	[43]	Escambia Bay bridges (FL) (1966) Piles in tidal zone	~30	26.4 - 2.84 (ave.)	~1.2%	<30	>30	[Limestone aggregates likely]	No significant corrosion. PR measurements -‘negligible corrosion’ Very low chloride diffusivity.
Q2	[43]	Florida Keys bridges (5) (1980-2) splash zone (FL)	18-20	76 nominal (see comments)	~2.4-4% at 50-76 mm depth	<6	6 - 9 +	Limestone coarse aggregate	
R1	[29]	Test specimens (immersed	30	20, 40, 70	> threshold	[15-25]	>30		Slag cement and alumina cement concretes
R2		in natural seawater)			$\gg$ threshold	[<15]	<30		OPC and high early strength, moderate heat concretes.
S	[58]	Offshore platform - Brent B (N)	~20	75	~0.07%	~20	$\gg$20	OPC + additives [Norway aggregates]	No external evidence of rebar corrosion
T1	[42]	Experimental beams in	17	10 min	1.8-2.2%	4-6	>17	OPC + some limestone aggregate	B2CL2 -
T2		laboratory		40 max	1.3-1.9%	8-12	>17		A1CL1 -
U1	[26]	Hathaway Bridge piles (76)	42	31 (mainly)-50	low	[~<35]	[<40]	River rock, OPC	Rust stains on ~10%, minor delamination <3%
U2		Pensacola Bridge piles (908)	43	23.3	~0.4-2%	[~<35]	[<40]	River rock, OPC	Rust stains on ~10%, minor delamination <3%
U3		Brooks Bridge (30)	39	29	low	[~<30]		Undefined, OPC	Superficial rust staining
U4		St George Island Bridge (15) All in FL(USA)	1	72-89	negl.	<1		22% FA, 8% microsilica + limestone	Superficial rust staining Note: River rock likely to be limestone.
V1	[59]	Test specimens (Cabo Raso (P)	2	15-30 mm	0.42%	0.8-0.9		OPC or similar	Coastal atmospheric exposure
V2		and La Voz (V)			0.89%	1.8-1.9			
W1	[10]	Arbroath, North Sea, UK balustrade (1000 samples)	63 (1943)	25	~1.9%	~20-63	[>30]	Seashells in mix	<10% replaced, rest no significant corrosion (2006)
W2			49 (1968)	25	~0.5%	[5 - 15]	[<25]		All badly corroded and severely cracked
W3			14 (1993)	25	~1.8%	[$\ll$10]	<10		Most badly corroded and severely cracked

The column for cement/concrete aggregate is grey where ever there was use of blast furnace slag cement or limestone or dolomite aggregates.

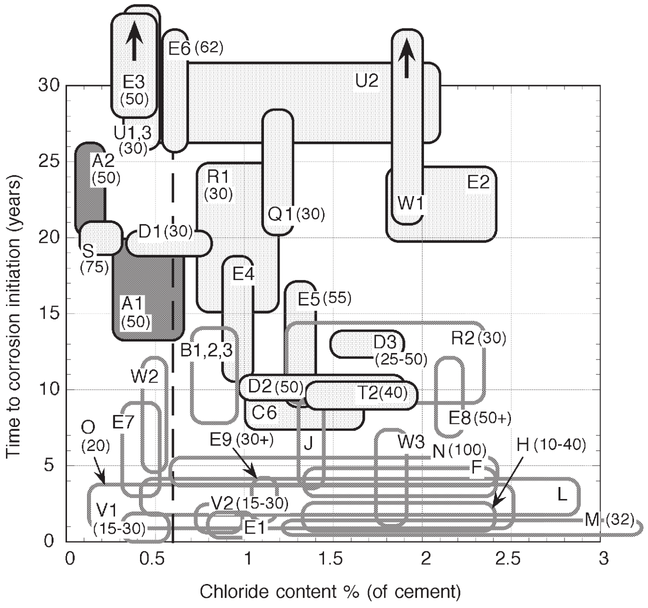

Fig. 2. Time t_i to corrosion initiation as a function of chloride content estimated at the level of the reinforcement for the cases shown in Table 1 for which information is available. Cases J and K, not shown, lie towards the bottom of the plot. Cover is 25 mm unless shown otherwise (in brackets, mm).

The data plotted in Fig. 2 has not discriminated for matters such as concrete cover and concrete permeability that could be expected to have some influence on initiation time. Unfortunately information on concrete permeability was available for only a few cases — insufficient to build a comprehensive picture of its influence. The nominal concrete cover for all data is 25 mm except where shown otherwise (in brackets, mm) in Fig. 2. Evidently, those cases with cover much greater than 25 mm tend to show lower chloride contents and longer initiation times, as expected. The fact that this is not always the case may simply reflect the uncertainty in some of the data relative to the initiation times of interest.

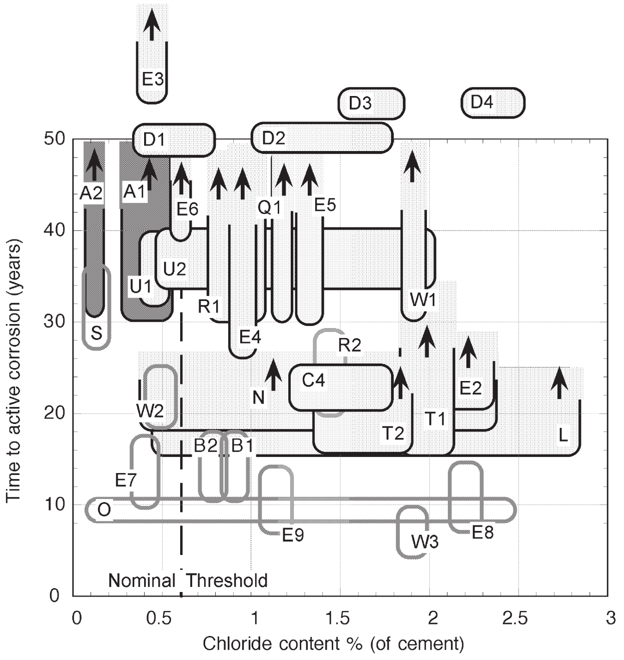

Fig. 3. Time t_{ac} to active corrosion as a function of chloride content estimated at the level of the reinforcement for the cases shown in Table 1 for which information is available.

For the time t_{ac} to active corrosion, Fig. 3 shows a clear distinction between the structures constructed from ordinary concrete and those in which the aggregates contained limestone, dolomite or other forms of calcium carbonate. The ordinary concretes all led to active corrosion occurring within about 20 years of exposure, somewhat longer when the chloride content was lower. For the concretes containing limestone, dolomite, seashells or blast furnace cements the time to active corrosion was at least 15 years after first exposure (case L) and in most cases very considerably longer, with some cases showing no sign of active corrosion even after 60 years exposure.

Fig. 3 does not discriminate for concrete cover. This is unlikely to have much influence on activation time since in most cases the reinforcement can be expected to be fully exposed to high levels of chloride (and moisture) in the surrounding concrete after 20 years or so.

5. Discussion

Fig. 2 shows clearly that in general the initiation time t_i was quite short, typically occurring within a few years of first exposure. However, there are also a number of cases for which the initiation time was considerably greater. Commonly such differences have been dismissed and attributed to differences in concrete composition, in concrete quality and in cover to the reinforcement. Undoubtedly these factors will have influences on long-term corrosion behaviour of reinforcement. However, their influence is not consistent, with some structures with poor quality concrete or minimal cover displaying better corrosion resistance than others with high quality concretes and greater concrete cover. This inconsistency has been noted before [9,24].

Within the limitations of the available information, the present analysis shows that with t_i and t_{ac} as defined herein (Fig. 1b) all of the longer t_i appear to be associated with the use of blast furnace slag cement or with some form of calcareous material for aggregates, such as seashells, limestone or (non-reactive) dolomite aggregates in the concrete. Similarly, the time t_{ac} to active corrosion is seen generally to be much longer for the concretes made with calcareous material or blast furnace slag cement. Moreover, the interval between t_i and t_{ac} is greater, typically, for the latter. These observations appear not to have been made previously.

From a scientific perspective the interesting question that arises is how the observed differences in t_i and t_{ac} between the various reinforced concrete structures might arise. Clearly, one possible reason for this may be the effect of the constituents of the concretes on chloride diffusion rates. Concretes made with blast furnace cements usually are considered to have greater resistance to inward chloride diffusion as a result of this cement reducing the diffusion coefficient. This was deduced from extensive field observations of their long-term performance compared with the performance of concrete structures made from ordinary Portland cement (OPC) [28]. Accelerated laboratory tests on various concrete specimens support this conclusion. For example, Arskog et al. [44] noted that the chloride diffusion coefficients all reduced significantly in the first 30–40 days after exposure and appeared to converge in value. Unfortunately the short 180-day test regime does not permit a conclusion whether this convergence is likely to continue for longer exposure periods. It obviously is a matter for further investigation. The tests did show that significant changes occur within the concrete matrix during the early exposure period, and possibly longer. The manner in which these changes differ from those observed for chloride diffusivity in OPC concretes appears to be unclear at this time.

One known mechanism that has an effect on the transport of chlorides into the concrete from the external marine environment is the deposition of aragonite (a form of calcium carbonate) and brucite (a form of magnesium carbonate) on the exterior surfaces of concrete continuously immersed in seawater [45]. Whether this effect extends also to tidal and atmospheric exposure conditions and whether it is somehow influenced by the presence of limestone or dolomite aggregates in the concrete mix or the use of blast furnace slag cement remains a matter for investigation. However, this mechanism may be the reason for the observation that the chloride profile does not appear to change much with time after some initial period (perhaps some years). For example, Cusson and Qian [24] found that 'the corrosion products at the steel surface did not progress significantly,' even over a period of 10 years. This may be related to the observed decease in diffusion coefficient with time (see above). Again, there appears to be no comparable test information for the effects of limestone or dolomite aggregates. In this respect the earlier test data reported by Matthews [46]) is too short and sparse to draw conclusions. There are clearly a number of related matters here for further investigation.

Despite the considerable developments in the theory of chloride diffusion and refinements beyond the simple application of Fick's law of diffusion, including allowance for the so-called 'skin effect' and chloride transport by absorption mechanisms [7], current theory is not always consistent with field observations (e.g. [9]). This may be illustrated by the predictions of Amey et al. [47] for the service life of concrete structures in the tidal and splash zones in Florida (compare with cases U in Table 1). Using an assumed 65 mm concrete cover, optimistic concrete properties and chloride penetration as the critical condition for time to initiation t_i. Amey et al. [47] estimated $t_i = 9$ years. Assuming that the time interval to significant damage ranges from 3 to 6 years depending on concrete resistivity and temperature, they estimated a service life of 16 years, extending to 27 and 33 years respective for a high quality concrete and concrete with 8% silica fume. However, the actual cover as reported by Lau et al. [26] for case U in Table 1 is only half of the 65 mm assumed. With the usual assumption that chloride penetration varies exponentially with depth it is easily deduced that the time to initiation for 30 mm cover would be about 4 years and the expected service life 9–10 years. Evidently, these estimates are very seriously less than the in-situ observations.

Since corrosion of reinforcement in concrete requires the presence of moisture, one potentially important variable not considered in the above analysis is fact that atmospheric moisture tends to be retained well within the concrete mass, irrespective of external fluctuations and therefore the reinforcement is likely to be wet most of the time if not continuously. This is likely to be the case for most of the structures in Table 1, particularly for structures in tidal regions, bridges, etc. exposed to coastal spray and wave action and bridges in wet climates such as the UK, or where de-icing salts are used for a significant part of the year. One example that does not fit this pattern is the inland footbridge described by Polder and Hug [40] for which de-icing salts were applied rather infrequently. In this case the time t_{ac} (as defined in Fig. 1b) is probably over-estimated compared to the average structure in Table 1. In contrast, the part of the bridge with the deteriorated coating probably retained moisture more than would have been the case under natural conditions, such that the value of t_{ac} probably is under-estimated. It follows that a more detailed analysis should consider 'time of wetness' as a parameter. However, this is likely to be difficult since, unlike corrosion studies for bare steel in marine environments, this parameter has almost never been reported for reinforced concrete structures.

Changes in cement making practice are sometimes proposed as responsible for the lower durability of reinforcement in modern concretes. Except in the USA where changes commenced already in the 1930s [48], changes in cement making (higher clinkering temperatures and finer grind) did not come about until the 1960s in most countries [33], yet concern about variability in reinforcement durability was documented already much earlier. Typically the reason advanced is that the finer grind cements produced concretes less able to bind chlorides. The information in Table 1 and Figs. 2 and 3 does not obviously correlate with these changes, even allowing for the delay in development of obvious symptoms. For example, there are a number of cases for which chloride contents were found to be very high yet there was little or no evidence of corrosion initiation. Where cement has been implicated a contributing factor may well be the likelihood that with higher early strength cements the need arose to use stronger aggregates and thus a trend to use igneous rock rather than limestone and, perhaps, (non-reactive) dolomite. If this is the case, the durability issue obviously is superficially but falsely correlated with changes in cement making.

In the analysis given in Table 1 and Figs. 2 and 3 it was necessary in many cases to make assumptions about the stone aggregates used in the concretes, as this was only seldom reported in the literature. Nevertheless it was reported in some cases and in others there can be little doubt about the most likely source(s) of concrete aggregates. Even though this may add a further dimension of uncertainty, the predominance of the trends in Figs. 2 and 3 suggests that this is not a major source of error. Further, since concrete mix data are only seldom reported, it has not been possible to perform an analysis of calcium carbonate content versus structural performance such as measured through t_i and t_{ac}. Such analysis will only be possible once these matters start being reported in the literature or when specifically designed experimental programs are put in place. In both cases it is clear that practical results will take a long time to become available. For this reason the historical approach adopted herein was considered the only practical way forward as well as highlighting a potential variable that, to date, appears to have been entirely ignored within the usual assumption that the aggregates are 'inert'.

Despite the information in Table 1 and Figs. 2 and 3 being subject to considerable uncertainty, as noted above, collectively it points to a consistent trend, namely that elevated levels of calcareous material in the concrete mix may be linked to enhanced durability of reinforcement against corrosion. The information used in Table 1 (and the trends in Figs. 2 and 3) suggests this inference but cannot validate it and this difficult task remains. Controlled long-term experiments with a range of concrete aggregates and identical exposure conditions were commenced (at Newcastle) in 2005 in an attempt to provide further insight and independent confirmation but clearly longer-term information may not be available for several decades.

6. Conclusion

For reinforcement in concrete structures exposed to marine environments or to de-icing salts the information presented herein shows that the time to corrosion initiation does not depend strongly on the reported concentration of chlorides at the reinforcement. For many structures this was less than 5 years. However, it was considerably greater for reinforced concrete structures constructed from limestone or (non-reactive) dolomite aggregates or with blast furnace cement. For these the initiation period was at least 10 years and in most cases greater than 15 years, with some much greater still.

Similarly, the time period to the commencement of active corrosion was found to be not strongly related to chloride content. For most structures it was less than about 20 years, consistent with anecdotal observations for many modern reinforced concrete structures. However, for reinforced concrete structures constructed from limestone or (non-reactive) dolomite aggregates or with blast furnace cement, it was considerably longer, ranging from about 17 years and in most cases to more than 30 years, with some extending to 60+ years. The precise exposure conditions appear to have only a secondary influence.

These observations have clear implications for the practical achievement of concretes with favourable long-term resistance to reinforcement corrosion. However, they need to be verified by controlled experiments or other detailed investigations.

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