

Admixed Chlorides in Concrete: History, Impacts, and Standardization

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Abstract: The presence of chlorides in cementitious materials results in corrosion of the embedded metallic materials. Early construction practices (pre 1960s) relied on admixed calcium chloride to accelerate the early strength gain of concrete. Until the 1950s, few publications focused on the effects of chlorides in concrete on corrosion and the use of chlorides was well established. However, in the 1960s significant publications reported on the effects of chlorides on the corrosion of prestressed wires and strands – these publications were the result of several failures of prestressed systems. Later, significant research was performed on the corrosion of steels in cementitious materials—a significant portion of this work attributable to the researchers being recognized in this symposium: Brian Hope and Morris Schupack. Their considerable efforts led to new knowledge regarding corrosion durability of reinforced and prestressed systems. Recently, ACI Committees 201 and 222 standardized limits on allowable admixed chlorides in the constituent materials. However, more standardization is needed—ACI Committees 318 and 349 report different admixed chloride limit requirements than Committees 201 and 222. This paper provides an overview of past research, analyzes the effects of chlorides on service life and economy and provides data from a research project. Using this information, the authors propose a standardized limit for chlorides in concrete.

Keywords: chlorides; corrosion; concrete; threshold; durability; service life; economic analysis

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INTRODUCTION

It is well known that chlorides cause premature corrosion of steel reinforcement in concrete. However, significant debate exists as to how chlorides initiate and propagate corrosion of the steel reinforcement in concrete, how much chlorides can safely be admixed³ in fresh concrete, and how much chlorides are needed to initiate the corrosion process. This paper will provide a simple overview of how chlorides initiate and propagate corrosion of steel reinforcement embedded in concrete. A review of the literature and specifying codes and how these documents evolved over time is then presented. This information is used to better understand the challenges associated with limiting admixed chlorides and how and why the existing limits were developed. Using the current limits for allowable admixed chlorides in concrete, a deterministic analysis of the effects of admixed chlorides on time to corrosion initiation and service life is provided. This is followed by an economic analysis that assesses the value of not using concrete constituent materials that contain chlorides. This analysis is followed by a section describing a small research test program that evaluated the corrosion activity of cementitious systems containing varying amounts of admixed chlorides. Using the information on the mechanisms of chloride induced corrosion, the history of admixed chloride limits in the literature and ACI documents, the effect of admixed chlorides on time to corrosion, service life and costs, and using the data obtained from the research, recommendations are made for standardizing limits on admixed chlorides.

MECHANISMS OF CHLORIDE INDUCED CORROSION

Chloride-induced corrosion of steel reinforcement requires that sufficient chlorides be present at the steel-cementitious materials interface. Chlorides can be introduced to the steel-cementitious materials interface via inclusion of chlorides into the fresh mixture or via transport through the cementitious system. When chlorides are included in the fresh concrete mixture, either from residual or contaminated constituent materials or intentionally added, these chlorides are immediately present at the steel-cementitious material interface, available for the corrosion

3. Admixed chlorides are defined in this paper as any chlorides that are present in the concrete during mixing. This can include chlorides naturally present in constituent materials (cement, aggregate, water, or supplementary cementing admixture) or from an admixture.

process. If present in sufficient quantities, these chlorides can initiate corrosion immediately; if present in less than sufficient quantities, these chlorides reduce the amount of transported chlorides needed to initiate corrosion. If sufficiently low or no chlorides are present in the cementitious system, all chlorides must be transported through the cementitious material to the interface. Because the transport (diffusion, permeation, convection, or migration) of chlorides through cementitious systems is a relatively slow process, the addition of chlorides to the fresh mixture can reduce the time to corrosion initiation of the steel reinforcement. Significant debate exists as to how much chlorides can be present in the fresh mixture and this topic will be addressed later. The point here is that chlorides are needed at the steel surface.

The corrosion resistance of steel is often related to the formation of a passive film. Passive films protect the base steel from reacting with constituents from the environment, thus improving its corrosion resistance. Very little research has been performed to assess the passive film on hot-rolled steel reinforcement. Steel reinforcement is generally produced using scrap materials. The scrap materials are melted and molded into billets. These billets are often stored and when needed, rolled at high speeds. The rolling process consists of continuously reducing the steel cross-section until the desired shape and size is achieved. Most steel mills hot roll the steel product under atmospheric conditions, resulting in the formation of a mill-scale on the surface of the steel. Mill-scale typically consists of iron oxides, often hematite or magnetite and can be both beneficial and detrimental to corrosion initiation and propagation. If the mill-scale is continuous and in compression, the scale acts as a barrier and is considered beneficial. If the mill-scale is in tension and discontinuous, the discontinuous sites are susceptible to accelerated corrosion because the protection from the mill-scale does not exist and because the mill-scale is cathodic to the base steel. Large cathodes to anode areas, as would be the case for breaks in the mill-scale, result in accelerated corrosion. Pillai and Trejo (2005), Mohammed and Hamada (2006), Mahallati and Saremi (2006), and Ghods et al. (2011) all reported that reinforcing steels containing mill-scale exhibited lower resistance to corrosion than polished steels, indicating that the current process of producing steels results in the mill-scale being discontinuous. Figure 1 shows typical surfaces for two commercially available reinforcing steels. These conditions make for variable corrosion.

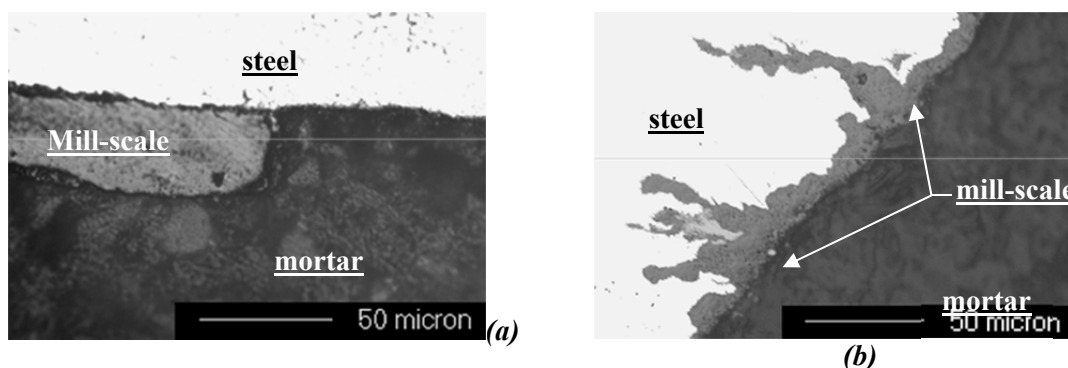


Figure 1—Micrographs of mill-scales for steel meeting ASTM specifications (a) A615 and (b) A1035

At locations where the mill-scale is discontinuous, a passive film likely exists. Passive films have been reported to be thin layers of oxides that occupy the reactive atom sites on the metal surface. By occupying these reactive sites, the film reduces the opportunity of metal atoms from reacting, thus preventing corrosion. Ghods et al. (2010, 2011a, 2011b) showed that the passive film on

steel in highly alkaline environments is approximately 5 nm (2×10^{-4} mils) thick and is composed of a thin and dense protective inner layer on the steel surface and a thick and porous outer layer. The inner protective layer was reported to be mostly composed of Fe^{2+} oxides and contained relatively smaller amounts of Fe^{3+} oxides. The outer layer contained relatively larger amounts of Fe^{3+} oxides than the inner layer. Other theories are also reported. However, this film is also likely heterogeneous, discontinuous, and its integrity and thickness vary with time before the chloride reaches the steel surface. Jones (1982) reported that corrosion initiation is likely a result of the electrostatic attraction between the positively charged metal surface (without an oxide layer) and the negatively charged chlorides. Hime and Erlin (1987) reported that the chlorides react with the unprotected ferric and ferrous ions to first produce ferrous chloride. The ferrous chloride then reacts with hydroxyl ions to produce iron hydroxide ($\text{Fe}(\text{OH})_2$), freeing the chlorides to further react with more ferric and ferrous ions. Janik-Czakor et al. (1975) reported that chlorides accumulate at the steel surface and form a hydrochloric acid below the accumulated chlorides. The porous iron hydroxide and the lower pH environment lead to localized corrosion. Figure 2 shows a schematic of the process. Note that water is converted to hydroxyl ions and the chlorides are released to further react with the base steel. This indicates that once chlorides react, they are always available for further reaction. This also shows that the availability of water is necessary for the reaction to continue.

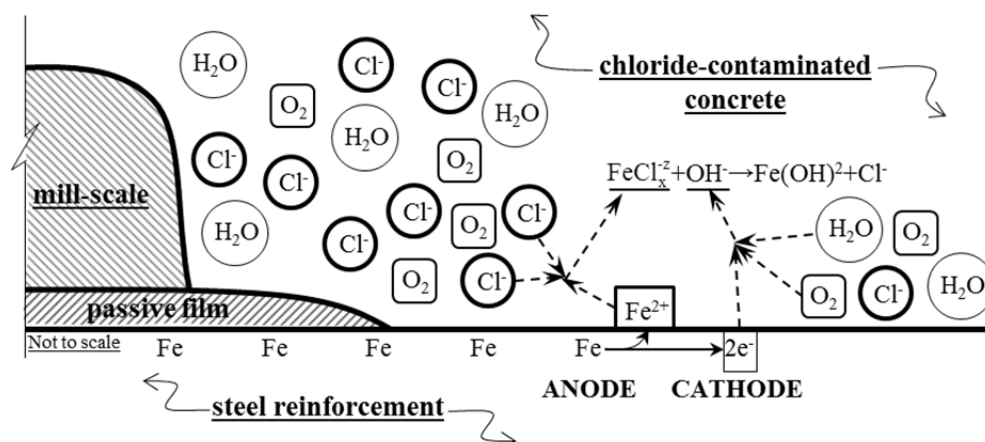


Figure 2—Simplified schematic of chloride-induced corrosion.

HISTORY OF CHLORIDE LIMITS

Chloride salts have been used in or on concrete for some time and the potential negative impacts of salt on corrosion were reported as early as 1924. Abrams (1924) reported when using seawater as mixing water for concrete that “in spite of satisfactory strength results, it seems unwise to use sea water in reinforced-concrete construction, particularly in the tropics on account of danger of corrosion of reinforcement.” In 1936, Gonnernan et al. reported on the effects of calcium and sodium chloride deicers on concrete performance and in 1939, Jackson and Kellermann reported on the potential use of chlorides as curing compounds. However, with the exception of Abrams reference, little was published early on chlorides and corrosion. In 1959, Shalon and Raphael performed a comprehensive study investigating the effects of sea water on corrosion of reinforcement in concrete. The authors concluded that “sea water used for mixing mortar or

concrete for air-exposed reinforced structures tends to make the reinforcement highly vulnerable to corrosion.” Further highlighting the potential challenges with chlorides in concrete, Monfore and Verbeck (1960) reported that calcium chloride should not be used in prestressed concrete. The work by Monfore and Verbeck was initiated mostly as a result of several corrosion failures of prestressed structures. However, the benefits of chloride as a deicer and accelerator had already been established (Rosenberg 1964). In 1965, ACI 604—*Recommended Practice for Cold Weather Concreting*, reported that “calcium chloride can be used safely as an accelerating admixture” but should not be used for prestressed concrete or when galvanized forms or decks are used. The document also noted that galvanic corrosion is intensified when calcium chloride is added to concrete. Hausman (1964) provided a good overview of corrosion of steel in concrete and later in 1969 Szilard reported that “reinforced and prestressed concrete bridges exposed to marine environment... frequently exhibit damage due to corrosion.” Szilard also noted that this corrosion was in part due to the seawater’s chloride content. Hausman’s and Szilard’s work further supported the concept that chlorides led to early and continued corrosion of reinforcement in concrete. However, in 1970, Tenaja reported that seawater could be used to make concrete if “proper mix design, quality, and workmanship” were employed. Later, Verbeck (1975) published a comprehensive article on the mechanisms of corrosion for steel in concrete and in the same year Erlin and Verbeck (1975) documented specific research needs to prevent corrosion for new and existing structures. The relationship between chlorides and corrosion was now clearly established.

Even with this knowledge, few limits were placed on using admixed chlorides in concrete. Even though there was some early (1904) work on corrosion of steel in concrete, the early ACI documents did not address the issue of chlorides and corrosion. ACI 318-47 (1949) made no reference to limiting chlorides in concrete and in fact, ACI 604-48—*Recommended Practice for Winter Concreting Methods* (1949) allowed the use “of small amounts of additional cement or accelerators such as calcium chloride to accelerate the hardening of the concrete at low temperatures (above 32 F) ...” The 318-47 requirement for water noted that water “shall be clean, and free from injurious amounts of oils, acids, alkalis, organic materials, or other deleterious substances.” ACI 318-63 modified the requirement for water to the following: “water used for mixing concrete shall be clean and free from injurious amounts of oils, acids, alkalis, **salts** (emphasis added), organic materials, or other substances that may be deleterious to concrete or steel.” The commentary for ACI 318-63 (1964) specifically noted that for prestressed structures, “calcium chloride or an admixture containing calcium chloride shall not be used” for concrete or grout. The document also specified that “seawater shall not be used” for prestressed concrete, however, no limits on the use of seawater in grout were specified. ACI 604-56 (1964) still allowed “calcium chloride to accelerate hardening of the concrete in cold weather” allowing 2% calcium chloride, except when sulfate-resisting concrete was required. Sulfate-resisting cements have low C₃A contents—Hope and Ip (1987) reported that cements and supplementary materials that contain higher C₃A contents have higher chloride binding capacities, thus reducing the potential for corrosion. More interesting, however, was a footnote added to the section on accelerators. The footnote noted that “another exception to use calcium chloride may be when there is reason to suspect that steel will be corroded by stray currents. In this event, an extra sack of cement should be used in preference to calcium chloride.” The footnote went on to discuss results from the *U.S. Bureau of Standards Technical Paper No. 18* (1913) reported in the *Highway Research Board Bibliography No. 13*, where “calcium chloride, even to the small extent of 0.03 percent, has been found to accentuate the effect of stray electric currents in

causing corrosion of iron.” The footnote further went on to note that “calcium chloride should not be used in prestressed concrete because of possible stress corrosion of the highly stressed special wire steel, but ordinary reinforcement is not affected.” Clearly, the cause and effect of chloride and corrosion had not yet made it into the code. ACI 604-56 noted that only 1 percent calcium chloride was the “minimum requirements for jobs taking maximum risk.”

The potential issues with chlorides in concrete had been established, but the ACI Committees were struggling with how or whether limits were needed for conventionally reinforced structures. The issue with limits on chlorides in prestressed structures was clear as several failures had occurred with prestressed structures that had chlorides admixed into the concrete. As such, ACI 201 (1970) reported that “calcium chloride and other soluble chlorides should not be used as admixtures in prestressed concrete.” The document also discussed the potential challenges of adding chlorides to concrete for structures exposed to marine conditions or conditions where “water-soluble salts” were present. Although caution was expressed, no limits on chlorides were presented for conventionally reinforced concrete structures. However, ACI 201 (1970) did place limits on the water-cement ratio and these limits were based on exposure condition and member type. For thin sections exposed to seawater, a maximum water-cement ratio of 0.4 (4.5 gallons per sack)—for moderate and thick sections the water-cement ratio could be increased to 0.45 (5.0 gallons per sack). Recommended water-cement ratios ranged from 0.4 to 0.53 (4.5 to 6 gallons per sack).

ACI 318-71 underwent significant changes from ACI 318-64. The former document prohibited the use of calcium chloride in both grout (for bonded tendons) and concrete and noted that “attention is called here to the possible adverse effects of excessive chloride ions in the presence of aluminum and, and in prestressed concrete.” The commentary also noted that “a new provision has been added concerning chloride ion content of water (including the portion of the mixing water contributed from the free moisture of aggregates) to be used in prestressed concrete or in concrete with aluminum embedment.” The commentary went on to note that “no numerical quantities are stipulated” but “it is suggested that chloride ion concentrations exceeding 400 or 500 ppm might be considered dangerous...” The commentary also noted that ACI 222 recommended levels well below these values and recommended that chlorides contained in the aggregate and admixtures should be considered in evaluating the acceptability of total chloride content in the mixing water.

ACI 318-77 included only minor revisions to the chloride limits established in ACI 318-71. Interestingly, the commentary noted that “**high** (emphasis added) concentrations of chloride ion may be harmful in prestressed concrete, because of possible corrosion, and in concrete containing aluminum...” The suggested levels of 400 to 500 ppm were replaced by “high.” Clearly, the Committee was struggling with the issue of chloride limits and corrosion.

ACI 201.2R-77 was one of the first ACI documents to detail challenges associated with chlorides and specifically addressed the issue of limiting admixed chlorides in the concrete mixture. The document noted the potential hazards of chlorides but noted that “specifying a zero chloride content for the mix, however, is impossible to realize in practice.” The 1977 document noted that “the threshold value for a chloride content in concrete necessary for the corrosion of embedded steel can be as low as 0.15 percent by weight of cement” but cautioned that this universal limit did not consider availability of chlorides, oxygen, and moisture. Interestingly, this chloride limit

seemed to be based on three references: two from studies on bridge decks and one on general corrosion of steel in concrete. A discussion was provided regarding “soluble” and “combined” chlorides, challenges with these different tests methods, and how these influence corrosion. More specifically, the 201.2R-77 document provided specific limits for chloride in concrete prior to service exposure based on total chlorides (i.e., free and combined chlorides). These limits were 0.06 for prestressed concrete, 0.10 for reinforced concrete in moist environment and exposed to chlorides in service, 0.15 for reinforced concrete in a moist environment but not exposed to chlorides, and no limits for above ground building construction that will stay dry—all chloride limits were based on weight percent of cement. The document noted that these limits were in agreement with ACI Committee 222, even though the 222 Committee would not publish its first document for another eight years. The 201 document also noted that calcium chloride should not be “intentionally added to the mix in prestressed concrete or conventionally reinforced concrete which will be exposed to moisture and chlorides in service.”

ACI 318-83 revised the requirements for chlorides to state that “calcium chloride or admixtures containing chloride from other than impurities from admixture ingredients shall not be used in prestressed concrete, in concrete containing embedded aluminum, or in concrete cast against stay-in-place galvanized metal forms.” This did not agree with the 1977 201 document that limited calcium chloride use to conventionally reinforced structures that were exposed to a dry environment with or without chlorides and to moist environments containing no chlorides. The 1983 318 code also published specific limits (based on weight of cement) on the chlorides based on structure type or exposure conditions—the beginning of a long dispute. The 318 code specifically noted that “for corrosion protection, maximum water soluble chloride ion concentrations in hardened concrete at an age of 28 days contributed from the ingredients” shall not exceed a specific weight percent of the cement. The published limits were 0.06 for prestressed concrete, 0.15 for reinforced concrete exposed to chlorides in service, 1.00 for reinforced concrete that will remain dry in service, and 0.30 for other reinforced concrete. The 1977 201 guide and the 1983 318 Code agreed on the 0.06 limit for prestressed concrete. However, the 1977 201 Guide recommended lower limits than the 1983 318 Code for reinforced concrete exposed to chlorides in service (0.10 versus 0.15) and for reinforced concrete exposed to moisture (0.15 versus 0.30). The 1983 318 Code was more conservative on chloride limits for dry conditions, requiring one percent maximum versus no limit for the 1977 201 Guide. The 1983 318 Code also placed a maximum water-cement ratio (0.40), a minimum strength (4750 psi [33 MPa]), and a minimum cover for corrosion protection of reinforced concrete exposed to deicing salts, brackish water, seawater or spray from these sources. Although progress was being made on limiting chlorides in concrete, variations in limits were leading to confusion.

In 1985 ACI Committee 222 published its first document on corrosion of metals in concrete and noted in the document that “placing limits on the allowable amounts of chloride ion in concrete is an issue still under active debate.” The document suggested acid soluble limits based on weight of cement of 0.08 for prestressed concrete and 0.20 for reinforced concrete. The Committee opted to specify chloride limits based on acid soluble testing because it was believed that acid soluble testing provided more consistent results than water soluble testing and because carbonation could lead to release of the chlorides (Tutti 1982). In general, the 0.08 limit was considered to be similar to the 0.06 limits reported by Committees 201 and 318 as water-soluble chloride contents were widely reported to be about 75 to 85% of acid soluble chloride contents (Hope and Poland 1987, Enevoldsen et al. 1994). The 222 chloride limits reported for reinforced

concrete were similar to those reported by 201 (75% of 0.20 is 0.15, where 0.15 is the limit in the 201 document). The 1985 222 document noted that “there are some exposure conditions where the chloride levels may exceed the recommended values and corrosion will not occur.” These conditions included submerged conditions where oxygen would not be available and cases where “concrete is continuously dry.” However, no limits were suggested for these cases. The 1985 222 document noted that its chloride limits differed from the values reported in the documents by Committees 201 and 318 and noted that “committee 222 has taken a more conservative approach because of the serious consequences of corrosion, the conflicting data on corrosion threshold values, and the difficulty in defining the service environment throughout the life of a structure.” In fact, the 222 limits could be considered to be less conservative than the limits published in the 201 document, but more conservative than the limits published in the 318 document.

ACI 318-86 attempted to further clarify limits on chlorides in concrete. First, the 1986 document specified testing for chlorides be performed on the hardened concrete of ages between 28 and 42 days (ACI 318-83 required testing at an age of 28 days). This document also defined that testing conform to test procedures described in Federal Highway Administration Report No. FHWA-RD-77-85, *Sampling and Testing for Chloride Ion in Concrete*. The commentary for ACI 318-86 also noted that the chloride limits were different than those published in ACI 222 and ACI 201. Table 1 shows a comparison of the limits published by the different ACI documents in 1987. The 318 code tended to take a less conservative approach to limiting chlorides than recommendations from Committees 201 and 222.

Table 1 Published chloride limits in concrete as reported by different ACI Committees

Exposure/Structure Type	Max Chloride (% weight of cement) Allowed in New Concrete as Published in 1986 ACI Committee Documents		
	201 (water-soluble)	222 (acid-soluble)	318 (water-soluble)
prestressed concrete	0.06	0.08	0.06
reinforced concrete exposed to chlorides in service	0.10	0.20	0.15
reinforced concrete exposed to damp exposure in service	0.15		0.3
reinforced concrete that will remain dry in service	1.0	higher than other 222 limits	1.0
reinforced concrete that is continuously submerged	Depends on whether exposure is to fresh or salt water – see above	higher than other 222 limits	Depends on whether exposure is to fresh or salt water – see above

The 1995 and 2002 318 Codes required the same limits published in Table 1. One significant difference between the ACI 318-86 and 318-95 codes were that allowable water-cement ratio (w/c) limits were changed to allowable water-cementitious materials ratio (w/cm) limits. The limiting values were in general the same values. The 1996 version of the 222 document included recommended limits for acid- and water-soluble chlorides. In addition, the 1996 222 document included a new test method for assessing water-soluble chlorides in the constituent materials. The limits published in the 1996 222 document are shown in Table 2 (these limits were also published in the 2001 and 2011 versions of the document). These limits varied significantly from the 201 and 318 limits published in 1986 and specifically noted that limits were “expressed as a percentage by weight of portland cement,” potentially implying that limits for w/cm were not

appropriate. In addition, the 1992 and 2001 201.2R document removed chloride limits and simply referred to levels reported in the 222R document. The 201.2R-08 document reprinted the 222 table limiting admixed chlorides. Committees 201 and 222 seemed to reach agreement on limiting admixed chlorides in concrete.

Table 2 Chloride limits published in ACI 222R-96, ACI 222-01, and ACI 222-11

Exposure/Structure Type	Chloride Limit for New Construction (by wt. of portland cement)		
	Acid-Soluble	Water-Soluble	
Test Method	ASTM C1152	ASTM C1218	Soxlet
prestressed concrete	0.08	0.06	0.06
reinforced concrete in wet conditions	0.10	0.08	0.08
reinforced concrete in dry conditions	0.20	0.15	0.15

In 2008, ACI 318 published a significant revision to the chloride limits. The document defined exposure classes for different exposure conditions. The document listed three classes: class C0 consisted of concrete that is dry or protected from moisture; class C1 (moderate exposure) consisted of concrete exposed to moisture but not to external sources of chlorides, and; class C2 (severe exposure) included concrete exposed to moisture and an external source of chlorides. Class C0 was to be assigned when exposure conditions do not require additional protection against the initiation of corrosion; C1 and C2 are assigned when additional protection is required, making the degree of protection dependent on the severity of the exposure condition. The 318-08 document specified maximum w/cm, minimum design strength (f'_c), minimum cover, and maximum chloride content. The limits from 318-08 are shown in Table 3. These limits are essentially the same limits from the earliest 318 document, but with defined exposure conditions.

Table 3 Chloride limits published in ACI 318-08

Exposure Class	Max w/cm	Min specific strength, f'_c , psi [MPa]	Max water-soluble chloride content in concrete, percent by weight of cement	
			Reinforced Concrete	Prestressed Concrete
C0	N/A	2500 (17)	1.00	0.06
C1	N/A	2500 (17)	0.30	0.06
C2	0.40	5000 (34)	0.15	0.06

In addition to the 201, 222, and 318 documents, Committee 349—*Concrete Nuclear Structures* provides limits for admixed chlorides in concrete. ACI 349-06 recommends a maximum water-soluble chloride content for corrosion protection of 0.06 percent by weight of cement for prestressed structures and 0.15 percent by weight of cement for reinforced concrete structures. These limits are higher than the 222 limits for “wet conditions” and the 201 limits for exposure “to chlorides in service,” and are the same as the 318 document for reinforced structures exposed to chlorides in service.

The 222R document is currently being revised. It is anticipated that limits could be recommended for different exposure classes. However, history shows that limits for reinforced concrete recommended by ACI Committee 222 have been consistently lower than those specified by ACI Committees 318 and 349. Limits for prestressed structures have been consistent over time, much of this justified based on research by Hope (1988 [with *Ip*] and 1994 [with *Enevoldsen and Hansson*]) and Schupack (1978, 1982, 1991, and 1998 [with *Stark*]). Care must be taken to balance risks associated with corrosion and costs associated with requiring low chloride levels. Additional costs could include using different and more expensive chemical admixtures, using different aggregate sources which could have higher material and transportation costs, using cleaner water, or others. In addition to costs, risks must be considered when making these decisions.

ASSESSING INFLUENCE OF CHLORIDES ON CORROSION

As noted in this paper, chlorides can have a significant influence on the corrosion activity of steel reinforcement embedded in concrete. The initial chloride limits published by ACI 201.2R-77 referenced three studies. Since this time, limited research has been performed to assess the influence of admixed chlorides and how these chlorides influence the corrosion activity of steel in concrete. A simple investigation was carried out to assess the influence of chloride content on the corrosion of reinforcement embedded in mortar containing various admixed chloride concentrations and exposed to water and saltwater environments. The following sections provide a theoretical assessment of the influence of admixed chlorides on corrosion, service life, and costs. This is followed by a brief description of the research program and results. It is anticipated that these sections will provide the reader with a better understanding of the potential impacts of admixed chlorides.

Theoretical Analysis of the Effects of Admixed Chlorides

The transport of chlorides into concrete towards the steel reinforcement is a complex phenomenon. Many studies have been performed to assess the rate at which chlorides are transported through the cementitious materials to the steel reinforcement, initiating corrosion of this reinforcement (Schießl and Wiens 1997, Weyers 1998, Liu and Weyers 1998, Li 2000, Li 2002, Zhang and Gjorv 2005). Pack et al. (2010) reported that the time-dependent transport of chlorides could be effectively modeled for bridge columns using simple diffusion models, assuming that the chloride surface concentration, C_s , and the apparent diffusion coefficient, D_a , are also time dependent. The authors noted that D_a decreases exponentially with time and C_s increases logarithmically with time and the chloride concentration at any depth and at any time, $C(x, t)$, can be determined as follows:

$$C(x, t) = C_s(t) \cdot \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D(t) \cdot t}} \right) \right) \quad (\text{Eq. 1})$$

where x is the depth of interest (length units), t is time (units dependent on units of diffusion coefficient), $C_s(t)$ is the time-variant chloride surface concentration, and $D(t)$ is the time-variant diffusion coefficient. Pack et al. (2010) reported that $C_s(t)$ and $D(t)$ could be estimated as follows:

$$C_s(t) = \alpha[\ln(\beta t + 1)] + k \quad (\text{Eq. 2})$$

$$D(t) = \frac{D_{ref}}{1-m} \left(\frac{t_{ref}}{t} \right)^m \quad (\text{Eq. 3})$$

where α , β , and k are constants reported to be 0.26, 3.77, and 1.38 for concrete containing portland cement, m is an age factor, t is the time of interest, and D_{ref} is the apparent diffusion coefficient at time t_{ref} , typically 28 days. Note that α , β , and k are dependent on environment.

Assuming aggressive conditions (as described in the paper by Pack et al.) where m is 0.06, D_{ref} is 2.02×10^{-9} in²/sec (1.3×10^{-12} m²/sec), t_{ref} is 28 days, a reinforcement depth of 2 inches (50 mm), the constants above are used to determine the time-variant chloride surface concentration, and the critical chloride threshold is 1.0 percent by weight of cement (a high value), the chloride concentration at the reinforcement depth as a function of time can be plotted for concrete containing different admixed chloride concentrations.

Figure 3 shows the chloride concentration as a function of time for concrete mixtures containing 0, 0.15, and 0.30 admixed chlorides by weight of cement. The time to corrosion initiation is approximately 32 years when no admixed chlorides are in the concrete mixture. When 0.15 and 0.30 percent chlorides by weight of cement are admixed in the concrete, the times to corrosion initiation are 25 and 20 years, respectively. Assuming concrete is placed with the limits allowed in ACI 318-08 (i.e., 0.15 and 0.30 by weight of cement), the time to corrosion initiation would be decreased by approximately 22 and 38% and the service life, assuming service life is the time to initiation plus 6 years, would be reduced by approximately 18 and 32%. These reductions are significant. If a slower rate of surface chloride is assumed (α , β , and k are 1.2, 0.1, and 0.01), the chloride concentration at the reinforcement level is shown in

Figure 4. The reductions in the time to corrosion are 8 and 15 years when 0.15 and 0.30 percent chlorides by weight of cement are allowed in the concrete. A 15 and 28% reduction in service life occurs when using the assumptions above.

The analysis indicates that chlorides levels of 0.15 and 0.3 can significantly reduce the time to corrosion and service life of reinforced concrete structures. The aggressiveness of the environment does not seem to be a significant factor in the percent reduction in service life as both conditions assessed exhibited similar reductions in time to corrosion (reduction of 7 and 12 years for the aggressive condition and a reduction of 8 and 15 years for the less aggressive condition). However, conditions where surface chlorides are not present would likely have a significant impact. It should be noted that this analysis is not comprehensive and cases can likely be found where a lower impact does occur—a comprehensive sensitivity analysis is warranted. However, the preliminary assessment indicates that admixed chloride levels that result in 0.15 and 0.30 percent water-soluble chlorides by weight of cement, as allowed by ACI 318-08, can significantly influence time to corrosion and service life and may be too high. It should be noted that the cathode to anode area ratio will impact corrosion initiation and propagation and this was not assessed in this study.

Knowing that admixing chlorides could reduce the service life of a reinforced concrete structure leads one to ask the question; how much cost is associated with this reduction in service life? If the cost associated with the reduction in service life is similar to the increase in construction costs associated with using materials that do not contain chlorides, then it may be justifiable from an economic perspective to use constituent materials that contain chlorides in the fresh concrete. Alternatively, if it is determined that there are significant costs associated with using materials containing chlorides, alternatives should be considered. Increase in construction costs could

include using higher costing admixtures that contain no chlorides, using imported aggregates or cementitious materials that have low or no chlorides, or using water that has no chlorides.

To quantify costs, a simple economic analysis can be performed. First, assume that the construction costs for a facility can at most be the present value of the income that can be generated from that facility. The construction costs, C_{constr} , then must be less than the present value of the income generated by the facility, $P_{facility}$, as follows:

$$C_{constr} \leq P_{facility} \quad (\text{Eq. 4})$$

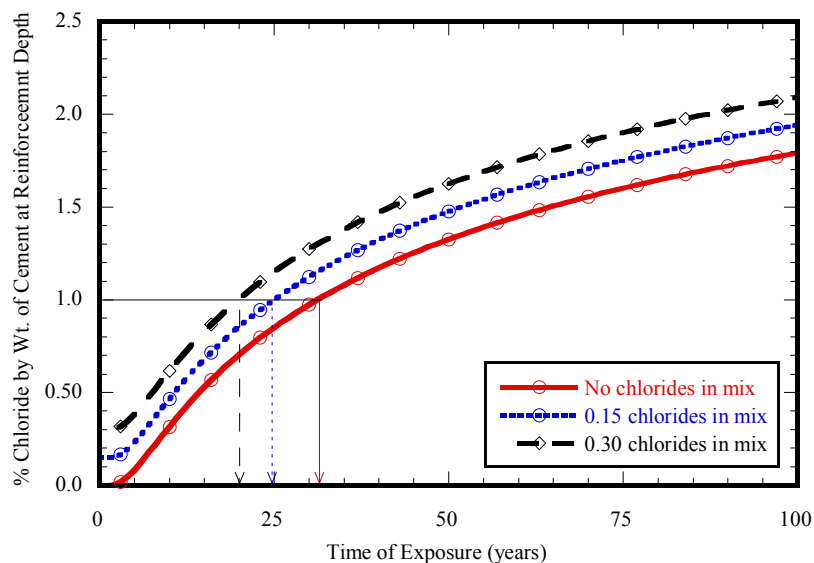


Figure 3—Chloride concentration at reinforcement level versus time for aggressive rate of chloride build-up at the surface

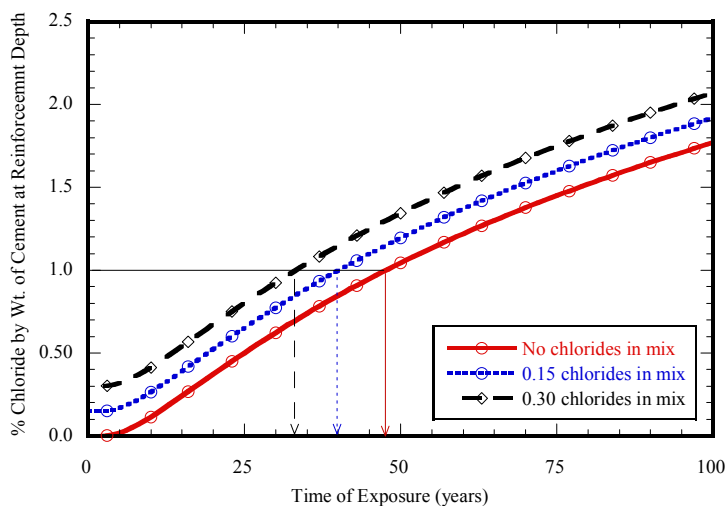


Figure 4—Chloride concentration at reinforcement level versus time for moderate rate of chloride build-up at the surface

Assuming that the owner or investors of the facility have two options: option A is to use constituent materials for the concrete that contain higher chloride levels that result in premature corrosion and a service life of n years; option B is to use constituent materials that will be more expensive but have limited levels of chlorides and a service life of $n+m$ years. Taking the ratio of these options results in the following:

$$\frac{C_{constr,B}}{C_{constr,A}} = \frac{P_{facility,B}}{P_{facility,A}} \quad (\text{Eq. 5})$$

Realizing that option B will generate more income over its lifespan than option A because it has a longer service life, it can be assumed that the maximum allowable percent increase in construction costs, $\% \Delta C_{max}$, to obtain the longer service life would be:

$$\% \Delta C_{max} = 100 \cdot \left(\frac{P_{facility,B}}{P_{facility,A}} - 1 \right) \quad (\text{Eq. 6})$$

Assuming that the facility for option A generates some regular annuity, A , over its service life, n , (see Figure 5) the present value, $P_{facility,A}$, for this option can be determined as follows:

$$P_{facility,A} = A \frac{(1+i)^n - 1}{i(1+i)^n} \quad (\text{Eq. 7})$$

where i is the rate of return. If the same structure is constructed with constituent materials that contain limited or no chlorides and the structure experiences an extended service life of m periods (months or years), the present value, $P_{facility,B}$, for this scenario would be:

$$P_{facility,B} = A \frac{(1+i)^{n+m} - 1}{i(1+i)^{n+m}} \quad (\text{Eq. 8})$$

Substituting Eqs. 7 and 8 into Eq. 6 and simplifying results in:

$$\% \Delta C_{max} = 100 \cdot \left(\frac{(1+i)^{n+m} - 1}{(1+i)^{n+m} - (1+i)^n} - 1 \right) \quad (\text{Eq. 9})$$

where m is simply the increase in time to corrosion (or service life). Figure 6 shows the $\% \Delta C_{max}$ as a function of time to corrosion, n , for a 2% rate of return and different increases in times to corrosion. If it is assumed that the time to corrosion for option A is 50 years and the time to corrosion for option B is 55 years, the ratio of the difference and the time to corrosion of option A is $0.1(n)$, or there is a 10% increase in time to corrosion from using concrete materials that

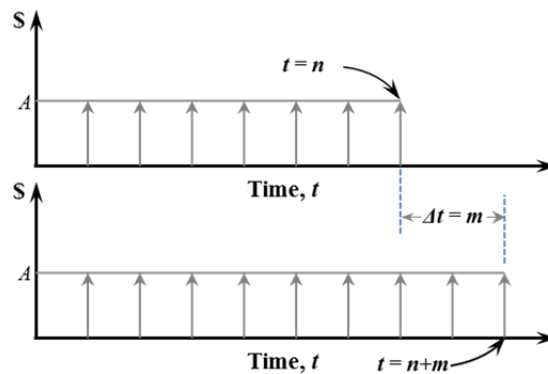


Figure 5—Cash flow diagrams for reinforced concrete structures with different service lives.

contain no chlorides. For this case, Figure 6 shows that construction cost can be increased up to 6% to eliminate the use of constituent materials that contain chlorides that increases the time to corrosion. Larger increases in time to corrosion lead to larger $\% \Delta C_{max}$ values. Assuming that a reinforced concrete facility costs \$10M to construct, a rate of return of 2%, a time to corrosion of 50 years when the concrete contains chlorides, and an increase in time to corrosion of 10% when the concrete does not contain chlorides, the owners or investors should be willing to spend up to \$0.6M ($0.06 \times \$10M$) to import the materials that contain no chlorides. This is a significant value for a modest increase in time to corrosion. Using the same assumptions but with increases in time to corrosion of 25% (12.5 years) and 50% (25 years), the owners or investors should be willing to spend up to ~\$1.3M and ~\$2.3M to import the materials that contain no chlorides. Figure 7 shows the similar plot but for a rate of return of 9%. Note that these values are lower than the values shown in Figure 6. This indicates that for public projects where rates of return are lower, significant benefits can be realized by using materials that contain limited or no chloride.

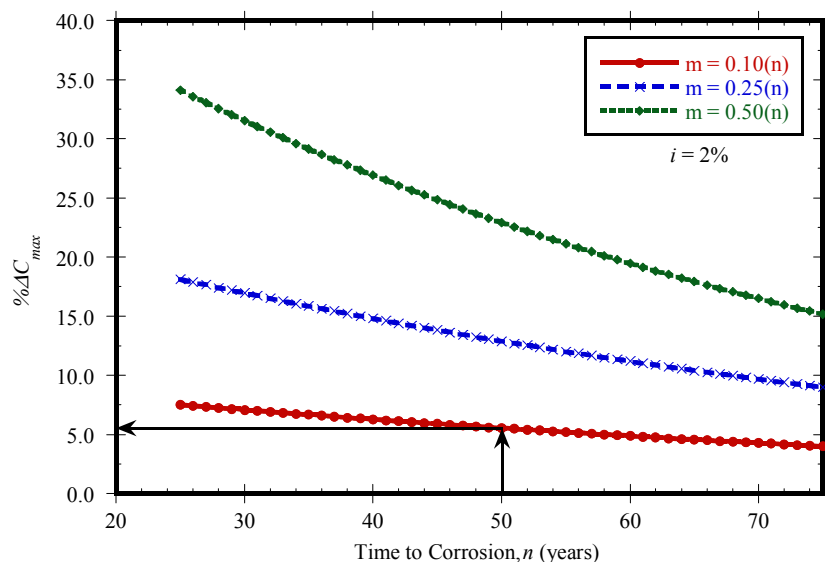


Figure 6—Maximum percent increase in construction cost for different times to corrosion and increases in time to corrosion ($i=2\%$).

Test Program to Assess the Influence of Admixed Chlorides on Corrosion

To assess the influence of admixed chlorides (chlorides mixed in the fresh mortar), a small study was performed. Small specimens, referred to as rapid macrocell (RMC) test specimens, were used to assess the corrosion performance of mortar containing different amounts of admixed chlorides. The RMC test was originally developed at the University of Kansas under the Strategic Highway Research Program (Martinez et al. 1990). Modified versions of the test method have been reported with the objective of improving the consistency and repeatability of the test. This program used mini lollipop samples with #5 (#16M) reinforcing bars centered in 1.1 inch (27 mm) diameter mortar specimens. The mortar specimens were 2.5 inches (63 mm) long and the reinforcing bar was 2.3 inches (58 mm) long. The reinforcing bar extended from the end of the mortar by 5/8 inch (16 mm). For each test, one specimen (the anode) was placed in the test solution (water or 5% calcium chloride solution) and two specimens were placed in a water

solution—these were the cathodes. The anode and cathodes were connected through a 10 Ω resistor and the electrolytes were connected with salt bridges. The macro-cell corrosion current was regularly monitored. The macro-cell current was assessed by measuring the voltage drop across the resistor using a voltmeter. The mortar had a water:cement:sand ratio of 0.45:1.0:2.25. A Type I/II cement was used and the fine aggregate was a natural sand with a fineness modulus of 2.2. The steel reinforcement met the requirements of ASTM A615 and ASTM A706.

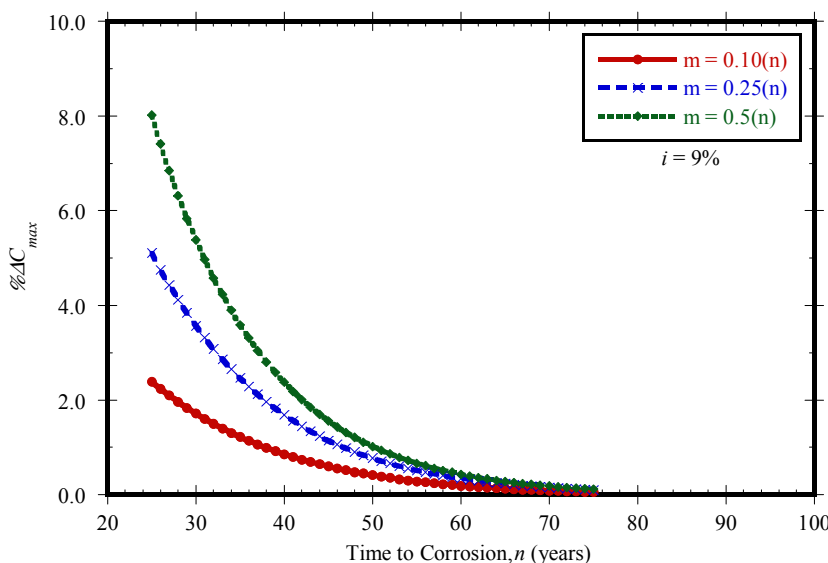


Figure 7—Maximum percent increase in construction cost for different times to corrosion and increases in time to corrosion ($i=9\%$).

Ten sets of specimens (1 anode and 2 cathodes; 30 specimens total) for each admixed chloride concentration and exposure condition were fabricated and assessed (210 specimens). Specimens were fabricated, cured for 28 days, then exposed to the solution. For the fresh water exposure, admixed chloride concentrations included 0.1, 0.15, 0.3, and 1.0% by weight of cement. Note that both the anode and cathodes contained the admixed chlorides, as this would be the case if chlorides were admixed into a concrete. For the salt water exposure, admixed chloride concentrations included 0.1, 0.15, and 1.0%. A total of 70 specimen sets were cast and assessed for corrosion activity. Exposure and data acquisition occurred over a period of approximately 170 days.

To better compare the results, the amount of cumulative coulombs passed were determined and plotted versus time. The macro-cell current was converted to coulombs simply by multiplying the macro-cell current by the test interval time, in seconds. Figure 8 shows results for the specimens subjected to the fresh water solution—due to space constraints, only the average value of the 10 specimens are shown. Figure 9 shows the results for the specimens subjected to the salt water solution. Again, only the average values of the 10 specimens are shown. The figures clearly show that increased concentrations of admixed chlorides increases the amount of coulombs passed (and thus the corrosion activity). Using these data, the mass, m , of the corroded reinforcing bars can be determined using the following:

$$m = \frac{C \cdot a}{n \cdot F} \quad (\text{Eq. 10})$$

where C is the coulombs passed at the end of the test, a is the atomic weight of steel (assumed to be 55.845 amu), n is the number of equivalents exchanged (2 for steel), and F is Faraday's constant (96,500 coulombs per equivalent). Note that this only accounts for macrocell current and microcell current will likely increase the mass loss due to corrosion.

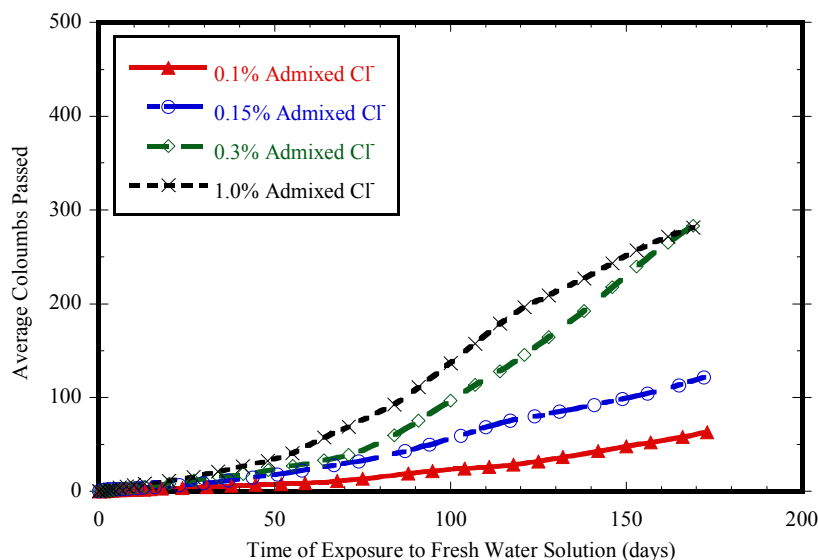


Figure 8—Corrosion activity for specimens containing different levels of admixed chloride exposed to fresh water

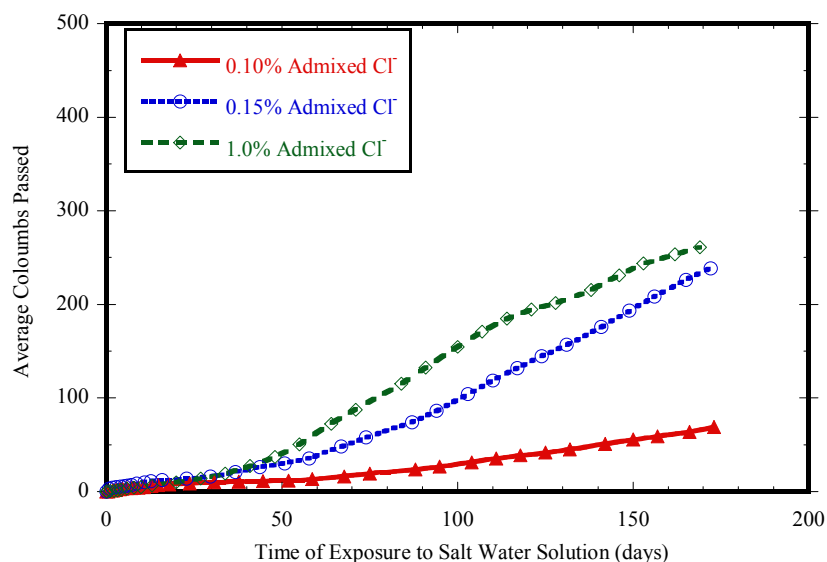


Figure 9—Corrosion activity for specimens containing different levels of admixed chloride exposed to salt water

Knowing the mass reacted, the average corrosion rate, r , can be determined as follows:

$$r = \frac{m}{t \cdot A \cdot D} \quad (\text{Eq. 11})$$

where t is the time of the test (in years), A is the surface area of the corroding specimen, and D is the density of the steel.

Table 4 shows the average mass reacted and the average corrosion rates for the specimens containing different admixed chlorides exposed to fresh and salt water. RILEM TC 154-EMC, Electrochemical Techniques for Measuring Metallic Corrosion, reported that corrosion rates less than 0.04 mils/yr (0.001 mm/yr) are considered as negligible, corrosion rates between 0.04 mils/yr (0.001 mm/yr) and 0.20 mils/yr (0.005 mm/yr) are considered to be low, corrosion rates between 0.20 mils/yr (0.005 mm/yr) and 0.40 mils/yr (0.01 mm/yr) are considered to be moderate, and corrosion rates above 0.40 mils/yr (0.01 mm/yr) are considered to be high. Table 4 also shows the corrosion level for each admixed chloride level and exposure condition.

Table 4 Corrosion data from experiments

	Exposure Condition							
	Fresh Water				Salt Water			
	Admixed Water Soluble Chloride				Admixed Water Soluble Chloride			
	0.1%	0.15%	0.30%	1.0%	0.1%	0.15%	0.30%	1.0%
Mass of Reinforcement Reacted, lbs. (gram)	4.0×10^{-5} (0.02)	7.8×10^{-5} (0.04)	1.8×10^{-4} (0.08)	1.8×10^{-4} (0.08)	4.4×10^{-5} (0.02)	1.5×10^{-4} (0.07)	NA	1.7×10^{-4} (0.08)
Average Corrosion Rate, mils/yr (mm/yr)	0.14 (0.003)	0.27 (0.007)	0.63 (0.016)	0.62 (0.016)	0.15 (0.004)	0.52 (0.013)	NA	0.58 (0.015)
Relative Corrosion Rate	Low	Moderate	High	High	Low	High	NA	High

The research clearly shows that increasing the amount of admixed chlorides increases the average corrosion activity of the specimens tested in this program. The results also indicate that even small amounts of admixed chloride can result in low levels of corrosion (as opposed to negligible corrosion levels). When chloride is admixed into the fresh cementitious materials and the water soluble chloride level is 0.15%, moderate and high levels of corrosion occurred in this experiment. In addition, with the exception of the 0.15% soluble chloride concentration, the mean corrosion rates for fresh and salt water were similar. For the 0.15% water-soluble chloride concentration, the salt water exposure led to a higher average corrosion rate.

SUMMARY, RECOMMENDATIONS, AND FUTURE RESEARCH NEEDS

Early research indicated that chlorides in concrete could lead to corrosion of the reinforcement. More recent research has clearly shown that chlorides do indeed result in corrosion, but the corrosion activity is dependent on local conditions at the steel-concrete interface and on the environment in which the concrete is exposed. Water and oxygen are requirements for chloride-induced corrosion and this corrosion is often highly variable. What has not been established is how much admixed chlorides should be allowed in the fresh concrete. Setting a limit of zero chlorides in concrete is not practical and would make concrete cost-prohibitive for most cases. However, it has been shown here that admixed chlorides can result in active corrosion and reductions in service lives. In addition, it has been shown that these reductions in service lives result in significant reductions in value.

Unlike ACI 201 and 222 documents, ACI 318 and 349 are code documents. These documents must consider the safety, construction costs, and life-cycle costs associated with initiating and propagating chloride-induced corrosion. In addition to chloride limits and exposure conditions, a structure's importance should be considered when recommending allowable admixed chlorides. The objective of this paper is not to provide specific definitions for corrosion levels or structure importance but to provide a general concept for establishing chloride limits in concrete. Examples of importance could be as follows: low importance could include structures that have a low hazard to human life if failure occurs; moderate importance could be structures that have some minimal hazard to human life if structural failure occurs, and high importance would be associated with structures that are either essential or would have higher hazard or risk to human life if structural failure occurred. Again, the point of this paper is not to argue about the definitions of low, moderate, and high corrosion or importance. The point of this paper is to note that limits are needed, these limits are dependent on environment and structure type, and these limits should be dependent on the importance of the structure. It is hoped that this paper will lead to further discussions such that limits on admixed chlorides can be established based on good science and research. This will allow for economical use of chlorides in concrete construction, while minimizing the long-term safety and economic issues associated with using chlorides in concrete.

Table 5 shows the authors recommendations for chloride limits. The authors believe that these values should be based on acid-soluble chloride levels as it has been well established that bound chlorides can become unbound during the service life (Enevoldsen et al. 1994, ACI 222R 2011). The authors believe that flexibility should be provided regarding maximum allowable admixed chloride limits, but these limits should not significantly decrease the safety or economy of structures made of concrete.

Table 5 Recommended chloride limits for all ACI documents.

Exposure Class	Importance	Max acid-soluble chloride content in concrete, percent by weight of cement	
		Reinforced Concrete	Prestressed Concrete
C0-Concrete that will be dry and protected from moisture	Low	0.40	0.06
	Moderate	0.30	0.06
	High	0.20	0.06
C1-Concrete exposed to moisture but not to external sources of chlorides	Low	0.15	0.06
	Moderate	0.10	0.06
	High	0.10	0.06
C2- concrete exposed moisture and an external source of chlorides	Low	0.10	0.06
	Moderate	0.10	0.06
	High	0.08	0.06

The concrete community has long struggled with setting limits on admixed chlorides, trying to balance initial and life-cycle costs. Very little research has been performed to understand the effects of admixed chlorides and more research is needed. Research needs include quantifying and assessing the impact of admixed chlorides on the time-variant corrosion activity of steel reinforcement (conventional and prestressed), assessing the time-variant damage and capacity loss to the structure resulting from this corrosion, and providing a better understanding of the

economic impact of this corrosion, damage, and loss of capacity. After our community resolves the issue of limiting admixed chlorides, we can move on to resolving the challenge of defining chloride threshold levels.

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Formation and Stability of Protective Passive Films formed on the New Generation of Stainless Steel Rebar Alloys

By B.P. Bergsma and C.M. Hansson

Synopsis: Electrochemical polarization and Raman spectroscopy were used to investigate the passive film formation of four grades of stainless steels in concrete and synthetic concrete pore solutions. Steels tested were austenitic grades UNS S24100 and UNS S31603, and duplex grades UNS S32101 and UNS S32304. These techniques have identified both similarities and differences in the protective films. The air-formed Cr_2O_3 film is not stable on any of the steels at potentials more anodic than approximately -100 mV SCE. In its stead, CrO_3 and mixed spinels form at more anodic potentials. The manganese-bearing grades (S24100 and S32101) exhibited Raman peaks attributed to manganese-bearing spinels, indicating that these steels form unique passive films. These films show similar stability and breakdown behaviour in chloride-free pore solutions; studies in chloride-bearing solutions are on-going.

Keywords: Stainless steel reinforcing bars, synthetic pore solution, cyclic polarization, Raman spectroscopy

Bergsma and Hansson

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INTRODUCTION

A new generation of stainless steel alloys has been developed for use as reinforcing bars for concrete. These new alloys are designed to provide the corrosion resistance required for 100-year service lives for structures in highly chloride-contaminated environments at a reduced material cost relative to that of traditional grades of stainless steel reinforcing bars.

New grades of stainless steel reinforcing bar include the duplex UNS S32101 (LDX-2101) and the austenitic UNS S24100 (Enduramet32 or XM28). These grades are similar to UNS S32304 (2304) and UNS S31603 (316LN), respectively, but feature significant reduction in nickel and molybdenum contents. All the alloys have low carbon to limit the possibility of the formation of chromium carbides during the hot rolling and, or subsequent annealing. Nitrogen is added, in part to provide the interstitial hardening normally provided by carbon and, in part, to increase the corrosion resistance (Grubb et al. 2005). Manganese is added to these alloys both as an austenite stabilizer (Grubb et al. 2005) (instead of most of the nickel) and to increase nitrogen solubility in the alloys (Grubb et al. 2005). Reducing nickel and molybdenum reduces the initial material cost of the new grades, since the price of nickel and molybdenum has been as much as 33 and 48 times that of iron (London Metal Exchange 2011a; b), while manganese is only 6 to 7 times the price of iron (Metal-Prices 2011).

Protection of stainless steels in neutral solutions is attributed to the formation of a chromium oxide passive film. However, Cr_2O_3 is only thermodynamically stable below a potential of about -55 mV standard hydrogen electrode, or -290 mV saturated calomel electrode (SCE) in the highly alkaline environment of concrete (Pourbaix 1974), as indicated by the potential/pH diagram in Figure 1. Typical half-cell potentials recorded for stainless steels in concrete and concrete pore solution are from the chromium oxide stability limit of -290 mV SCE to -50 mV SCE (Garcia-Alonso et al. 2007; Hartt et al. 2009; Islam 2010), which is the above the range of stability of chromium oxide (Cr_2O_3) or the hydrated product, chromium hydroxide ($\text{Cr}(\text{OH})_3$). For potentials above the stability limit of the chromium species, hydroxides of nickel, iron and molybdenum (Pourbaix 1974), as well as an iron-nickel spinel-type oxide (NiFe_2O_4) (Beverkog and Puigdomenech 1999) are possible. Spinel are oxides of the form $\text{M}^1\text{O}-\text{M}^2_2\text{O}_3$, where the metallic ions M^1 and M^2 can be either the same or two different metals; these are presented as M_3O_4 or $\text{M}^1\text{M}^2_2\text{O}_4$. The term “mixed spinels” refers to products incorporating three or more metallic ions in an ambiguous mixture of oxides.

The long-term stability of the protective oxides and the development of other protective species on these steels in concrete do not appear to have been investigated.

In ongoing tests on uncracked concrete beams exposed to high concentrations of chlorides, the new stainless steels have remained passive for almost three years. However, corrosion was observed for one S24100 specimen after approximately six months of exposure to chlorides in cracked concrete prisms exposed to the same chloride environment. Although the initiation time for corrosion of the stainless steel in the cracked beam was more than ten times that of black steel in the same test, and its subsequent corrosion rate was found to be merely a fraction of that of black steel, concerns have been raised about the long term performance of these steels (Hartt et al. 2009; Islam, Bergsma & Hansson 2012).

If the corrosion resistance in concrete offered by UNS S31603 or UNS S32304 (beyond that of pre-existing chromium oxide) is due to nickel and/or molybdenum oxide species, the long-term protection of the newer grades may be significantly reduced.

In the present work, the stability of the air-formed passive film and the films formed at high pH were investigated using potentiodynamic cyclic polarization and Raman spectroscopy in synthetic pore solution with and without chlorides. This work builds on the knowledge gained from other researchers who have used cyclic voltammetry (Veleva et al. 2002) and X-ray photoelectron spectroscopy (XPS) (Veleva et al. 2002; Addari et al. 2008) to identify the nature and thickness of the films on stainless steel. An advantage of Raman spectroscopy over XPS is that it can be conducted with the specimen in-situ in the solution and while held at different electrochemical potentials. A disadvantage of Raman is that the penetration depth is dependent on absorption of light in the sample and it may not have the depth resolution of XPS (1-10 nm); however, the bulk metal matrix does not contain ionic and covalent bonds, and is only detected as fluorescence in Raman spectroscopy, while distinct peaks are generated for ionic and covalent bonds present at the surface.

EXPERIMENTAL PROCEDURE

Stainless steels examined were: UNS S24100, UNS S31603, UNS S32101 and UNS S32304. All steels were supplied as 16 mm (0.63 in) diameter, hot rolled, deformed bar. Compositions of the steels, acquired using X-ray fluorescence, are shown in Table 1.

Table 1: Stainless rebar compositions, as determined by XRF

Steel Types	Fe	Cr	Ni	Mo	Mn	P	S	Si
UNS S31603	67.1	16.5	9.7	2.1	1.4	0.08	not detected	1.1
UNS S24100	68.0	16.9	2.3	0.1	11.9	not detected	not detected	0.4
UNS S32304	70.3	21.5	4.7	0.3	0.9	0.04	0.06	0.8
UNS S32101	70.1	21.2	1.2	0.3	4.6	0.04	0.08	1.5

Table 2: Synthetic pore solution composition (Marcotte 2001)

Compound	Quantity (g/L H ₂ O)
Sodium hydroxide (NaOH)	5.27
Potassium Hydroxide (KOH)	18.5
Calcium Sulphate (CaSO ₄ · 2H ₂ O)	0.57
Calcium Hydroxide (Ca(OH) ₂)*	2.35

* Excess amount to maintain saturation

Samples for cyclic polarization were prepared by drilling and tapping 75 mm (~3 in) lengths of each steel for a stainless steel machine screw (for electrical connection). Then both ends were coated with epoxy and sealed with heat-shrink tubing, leaving 50 mm (~2 in) length of reinforcing bar exposed.

The specimens were immersed in pore solution, the composition of which is shown in Table 2, and allowed to stabilize for two days. Thereafter, their open circuit potentials were recorded and cyclic polarization studies were carried out. Tests were conducted by scanning from 50 mV below the open circuit potential (E_{corr}), up to +500 mV saturated calomel electrode SCE, and then returning to -400 mV SCE at a rate of 0.167 mV/s, as recommended by ASTM (ASTM G5-94).

An additional scan was performed on each sample after the open circuit potential had stabilized following the end of the previous scan, typically about 12 hours. This was to allow comparison between the polarization curve for the initial air-formed passive film with the polarization curve generated when this film was first cathodically removed during the cathodic portion of the previous polarization scan, and the new passive film subsequently formed in the pore solution. Previous studies have shown that the ASTM recommended scan rate of 0.167 mV/s is too fast for detailed analysis of the behaviour of steel in concrete. Therefore, a third scan was performed on a new sample of the same alloy at 0.01 mV/s in order to observe the effects of scan rate.

Corrosion products produced on a sample of S24100 in a parallel, long-term test were analyzed using powder X-ray diffraction (XRD) and X-ray fluorescence (XRF). Wet corrosion product was collected from a bar of the steel after exposure in a synthetic pore solution containing 15 wt% sodium chloride (~9 wt% chloride), air dried, and then finely ground. XRF was performed on the dried product in order to determine the composition.

The dried corrosion product was then subjected to XRD. The composition found through XRF analysis was used to identify appropriate peaks to compare with the XRD spectra.

In-situ Raman spectroscopy was performed on samples of the steels in chloride-free pore solution (clean pore solution), as well as in pore solution with 15 wt% chloride, added as sodium chloride (contaminated pore solution). A concentration of 15 wt% chloride in solution corresponds to approximately 7.5% by weight of cement in concrete (Bergsma 2009). Due to space restraints in the test chamber for the Raman spectroscopy, samples for these tests were prepared by cutting a 6 mm (0.25 in) length of bar, and grinding the cross-sectional face with 320 grit silicon carbide paper. For samples subjected to polarization, an electrical connection wire was soldered into one end. The soldered connection was coated to isolate the connection and any crevices from the solution and the effects of polarization. Separate samples of each steel were pre-conditioned using each of the following (4) techniques:

Sample (a) for four weeks at open circuit in clean pore solution,

Sample (b) cathodically cleaned at -300 mV vs. open circuit potential for 24 hours and then left at open circuit potential for four weeks in clean pore solution,

Sample (c) for three weeks at open circuit followed by one week polarized at +200 SCE in clean pore solution,

Sample (d) for two weeks at open circuit in clean pore solution, followed by two weeks with 15 % Cl^- as NaCl added to the solution, all at open circuit.

Raman spectroscopy was performed in situ, using a 633 nm laser. Samples were transferred from the pore solution cells to a petri dish with about 1 mm (0.04 in) of their pore solution covering the ground face of the sample. The test setup is shown in Figure 2; the sample, in the petri dish is placed on the microscope stage, and the chamber is closed to block external light.

RESULTS

For all the steels tested in cyclic polarization, the open circuit potential was between -250 and -150 mV SCE. This is more anodic than the thermodynamic stability limit of Cr_2O_3 which would result in gradual dissolution of the air-formed passive film on the steels. The cyclic polarization curves for the four steels exhibited very similar features albeit shifted to slightly different corrosion rates and potentials, as illustrated in Figure 3. For the sake of clarity, only the positive sweep of each of the curves is shown in Figure 3, but the reverse sweep was typical of passive steels and occurred at lower current densities than those of the positive sweeps. These curves indicate that the two austenitic steels S31603 and S24100 have similar corrosion rates and similar current densities after the peak value at +150 mV SCE. In contrast, the two lean duplex steels, S32101 and S32304 have higher corrosion rates and generally higher anodic currents.

The S24100 steel is used as an example in the following analysis and figures. Figure 4 shows two polarization scans: the first is for the S24100 steel after exposure to the solution for 48 hrs. The second scan was taken after the same specimen had been at open circuit for 12 hours following the first scan. The repeated cyclic polarization shows a more anodic open circuit potential (E_{corr}) and there is no minor peak at +360 mV SCE. This indicates that the air-formed film, stable at the open circuit potential in pore solution, is different than that reformed after anodic polarization.

The effect of scan rate is illustrated in Figure 5 which shows the polarization scans at 0.01 mV/s and 0.167 mV/s. These curves appear to be similar; however, the minor peak has shifted from +360 mV SCE in the faster scan to +285 mV SCE in the slower scan. Moreover, the corrosion current density obtained at the slower scan rate is approximately an order of magnitude lower than that at the higher rate in the potential range of +0.150 to +0.450 mV SCE.

The corrosion products analyzed by XRF and XRD were generated on a bar of S24100 immersed in a ~9 wt% chloride pore solution for 15 weeks. The bar was connected to two similar bars in chloride-free pore solution through a resistor, and the cells were ionically connected via a salt bridge to encourage macrocell corrosion of the steel.

The results of XRF conducted on this corrosion product are given in Table 3.

Table 3: XRF of S24100 corrosion product

Element	wt%
Fe	73.0
Cr	14.2
Mn	8.0
Ni	3.0

The XRD spectrum, not shown, had peaks corresponding to Goethite ($\alpha\text{-FeOOH}$), a common product of corroding black steel in this environment, the spinel magnetite (Fe_3O_4) and mixed spinels (e.g. FeMn_2O_4 , MnCr_2O_4 and NiMn_2O_4), all of which have very similar peak values. The NiMn_2O_4 spinel best matched the observed peaks. Raman spectroscopy during anodic polarization was attempted, but was found to be problematic because high corrosion rates produced suspensions of solid corrosion products in the test solution. Therefore, the spectra of condition (c) below were obtained with the samples disconnected from the potentiostat following polarization. The various Raman spectra are illustrated in Figures 5-8. Each figure shows the spectra for specimens exposed to synthetic pore solution:

- (a) four weeks at open circuit;
- (b) cathodically cleaned for 24 hrs. and left at open circuit potential for four weeks;
- (c) three weeks at open circuit followed by one week polarized at +200 SCE and
- (d) two weeks at open circuit followed by two weeks with 15 % Cl as NaCl added to the solution.

A summary of the peaks from these figures is given in Table 4. There are only a few peaks common to the four steels, notably at (i) 1085 cm^{-1} (probably CaCO_3 or FeCO_3 (Neff et al. 2004; Dunnwald & Otto 1989), (ii) 1640 cm^{-1} (which is attributed to carbon contamination by Oblonski & Devine (Oblonski & Devine 1995) or, for those specimens exposed to chlorides, hydrated chlorides (Ramya et al. 2010), and (iii) two peaks in the $3200 - 3370$ range attributed to the OH bond (Colthup & Daley 1990).

There are peaks at 1430 and 1450 in the two manganese-containing steels which do not appear in the spectra of S31603 or S32304, identified as maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Ohtsuka et al. 1986) or some form of manganese oxide. However there is another peak identified by Oblonsky as $\gamma\text{-Fe}_2\text{O}_3$ which only appears in the non-manganese bearing steels (at $704/715\text{ cm}^{-1}$). It is possible that this is another form of Fe_2O_3 . There are also three peaks unique to the S32101 alloy at 468, 605 and 1340 cm^{-1} identified as δFeOOH , MnCr_2O_4 and $\text{Fe}(\text{OH})_3$ respectively. On the other

hand, there are two peaks, identified as Ni(OH)_2 and $\gamma\text{-Fe}_2\text{O}_3$ in the S31603 and S32304 which do not appear in the S24100 and S32101.

Table 4: Summary of compounds and unidentified peaks from Raman spectroscopy (peaks in cm^{-1} , preconditioning indicated for peaks)

S31603	S24100	S32304	S32101	Compound	
276 ^{bcd}	270 ^{bd}	270 ^{abc}	270 ^a	OH bond	(Colthup & Daly)
		355 ^b		$\text{Cr}_2\text{O}_3/\alpha\text{Ni(OH)}_2$	(Desilvestro et al. 1988)
368 ^c	360 ^{acd}			$\text{Fe}_3\text{O}_4/\gamma\text{Fe}_2\text{O}_3/\text{FeCr}_2\text{O}_4$	Magnetite/Maghemite/ Chromite (Marcotte)
	395 ^c			MnCr_2O_4	(Lutz et al. 1991)
			468 ^c	$\text{Ni}_2\text{O}_3/\delta\text{FeOOH}$	Feroxihiite (Marcotte)
582 ^{cd}	575 ^{cd}	579 ^{bc}	580 ^c	CrO_3	
			605 ^c	$\text{MnCr}_2\text{O}_4/\text{FeCr}_2\text{O}_4$	(Lutz et al.)
715 ^{bcd}		704 ^{cd}		$\text{Ca(CO)}_3/\gamma\text{Fe}_2\text{O}_3$	(Boucherit et al. 1989)
1085 ^{abcd}	1085 ^{abcd}	1085 ^{abcd}	1085 ^{abc}	$\text{CaCO}_3/\text{FeCO}_3$	(Herman et al. 1987; Neff)
		1316 ^{acd}		$\gamma\text{FeOOH}/\alpha\text{Fe}_2\text{O}_3$	Lepidocrocite (Boucherit et al.) Hæmatite (Ohtsuka et al.)
			1340 ^{ab}	Fe(OH)_3	(Dunnwald & Otto)
	1430 ^{ab}		1450 ^{ab}	$\gamma\text{Fe}_2\text{O}_3$	Maghemite (Ohtsuka et al.)
			1527 ^a	X1	<i>unidentified</i>
		1575 ^{ad}	1580 ^{ab}	X2	<i>unidentified</i>
1600 ^{abcd}	1620 ^{abcd}	1630 ^{abcd}	1630 ^c	Hydrated Cl/ Carbon contamination	(Ramya et al. 2010)/ (Oblonsky & Devine)
		2655 ^a	2640 ^a	X3	<i>unidentified</i>
			2850 ^{ab}	X4	<i>unidentified</i>
3220 ^{abcd}	3225 ^{abcd}	3243 ^{abcd}	3265 ^{abc}	OH bonds	(Colthup & Daly)
3360 ^{abcd}	3360 ^{abcd}	3360 ^{abcd}	3370 ^{abc}	OH bonds	(Colthup & Daly)

DISCUSSION

The electrochemical polarization curves were typical of those generally observed for passive metals which, on reversal of the anodic applied potential, exhibit a decrease in current density and an open circuit potential at more anodic potentials than the original values. This is considered to indicate an increase in the protective nature of the surface. By reversing the potential to cathodically reduce any film, the metal usually assumes a new, more negative open circuit potential. However, the open circuit potential after cathodic polarization stabilized at a similar value to the original open circuit potential in the solution. This indicates that a protective film re-formed very rapidly in this high pH solution.

As the potential is increased anodically, the current density increases much more rapidly than it does for black steel under similar conditions albeit starting at lower current densities (Jaffer, Olsen and Hansson, Bertolini and Gestaldi 2011). Thus, for all the steels, the current density increased by almost three orders of magnitude from E_{corr} to a maximum value at potentials ranging from $\sim +50$ mV to $\sim +200$ mV SCE, as shown in Figure 3. It should be noted that the maximum current densities for the two duplex steels (S32304 and S32101) was approximately an order of magnitude higher than that for the austenitic steels (S31603 and S24100).

The Raman spectra for all of steels, after polarization at $+200$ mV SCE for one week, exhibited a peak which was not present in specimens originally held at open circuit potential and corresponds to either CrO_3 or mixed spinel. No Cr_2O_3 peaks were observed in these specimens, confirming the instability of this phase and in qualitative agreement with the XRD analysis of the corrosion products of S24100.

On increasing the potential to more anodic values than $+200$ mV SCE, the current decreased slightly indicating that the spinels are provided greater resistance to leakage current. The increase at potentials greater than $+500$ mV SCE can be attributed to the breakdown of the stable Fe_2O_3 oxide.

The polarization curve for S24100, however, exhibited a second “peak” in current density at $\sim +360$ mV SCE. For the first scan shown in Figure 4, the current increased sharply, suggesting that the CrO_3 or a mixed spinel was less stable. The decrease in current density at slightly more positive potentials implies transformation to another species.

When the scan was repeated on the same specimen after it had been at open circuit for 12 hours, the peak in current density at $+360$ mV SCE was not observed; this suggests that some other species is present when the new scan begins, rather than the air-formed film, and that it remains stable in this potential region.

At a slower scan rate, the second “peak” occurs at $\sim +285$ mV SCE and the current was approximately an order of magnitude lower than that observed at higher scans, indicating the formation of a more protective oxide/hydroxide layer when the alloy had a longer exposure at the anodic potentials. This behaviour would be more indicative of that observed in the Raman spectroscopy, in which the specimen was held at a constant anodic potential for at least 15 minutes.

The increase in current around $+500$ mV SCE during anodic polarizations was consistent whether studying the air-formed films or reformed films; reformed films did not show a reduced breakdown potential. This does not indicate any loss of protection when thermodynamically stable oxides form on the new steels in concrete after extended exposure. However, the Raman peaks that were unique to the new grades were not consistently detected with chlorides present in the solutions, indicating that they are not protective in contaminated concrete; further study of the effects of chlorides on these oxides is required to make any further conclusions.

CONCLUSIONS

The response of stainless bars to cyclic polarization in synthetic pore solution demonstrated that the original air-formed oxide was initially protective, but since it is not stable, it was eventually replaced by other, more thermodynamically stable species, identified as mixed spinels. Raman spectroscopy confirmed that the air-formed oxide species present on the steel when first exposed to pore solution are different from those formed after anodic polarization. The Raman spectra showed that all steels formed CrO_3 at anodic potentials. Some peaks which are unique to the manganese-bearing steels, probably either MnCr_2O_4 or MnNi_2O_4 , develop on the new alloys. The different protective films on the steels resist anodic breakdown during cyclic polarization in non-contaminated pore solution to similar transpassive potentials, indicating similar protective capacity. The long-term stability of these protective films in the presence of chlorides has not been determined. It is important that the long term stability of oxides in both non-contaminated and chloride-contaminated concrete be further characterized; cyclic polarizations in chloride-contaminated pore solutions are in progress.

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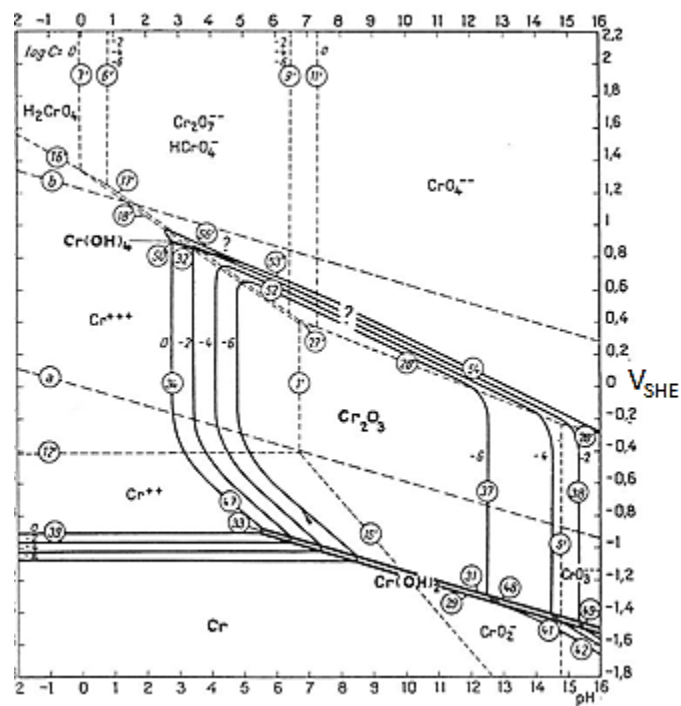


Figure 1: Pourbaix diagram for chromium

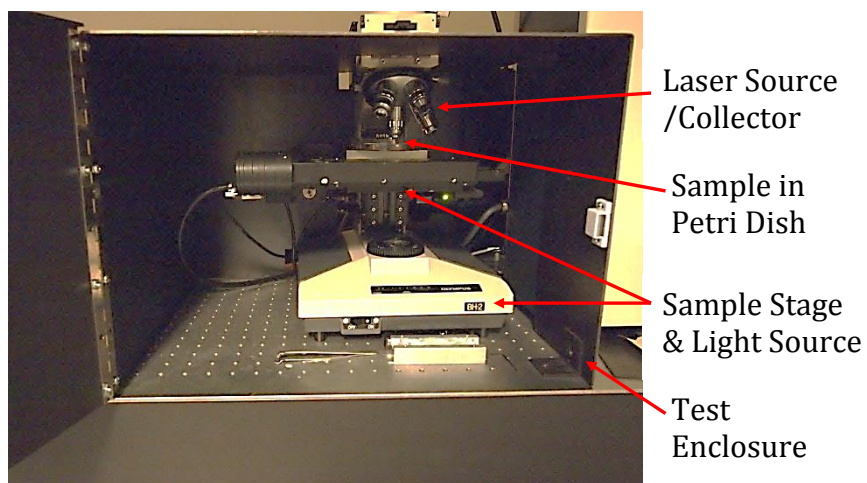


Figure 2: Raman spectroscopy setup

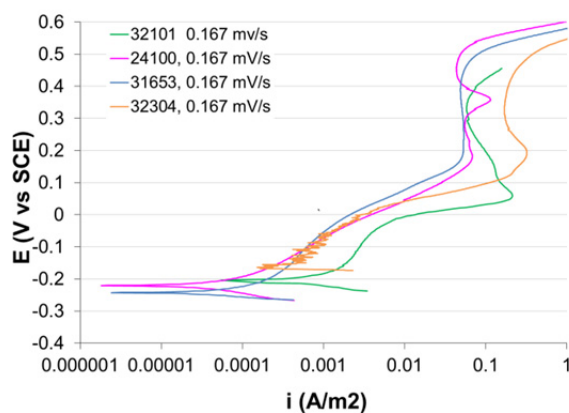


Figure 3: Anodic cyclic polarization curves for all steels at 0.167 mV/s

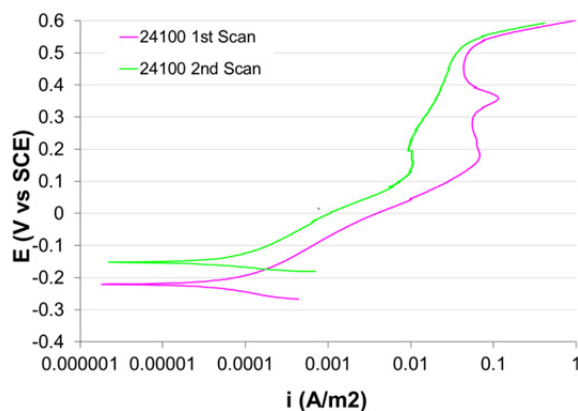


Figure 4: Cyclic polarization curves for UNS S24100 steel at 0.167 mV/s scan rate

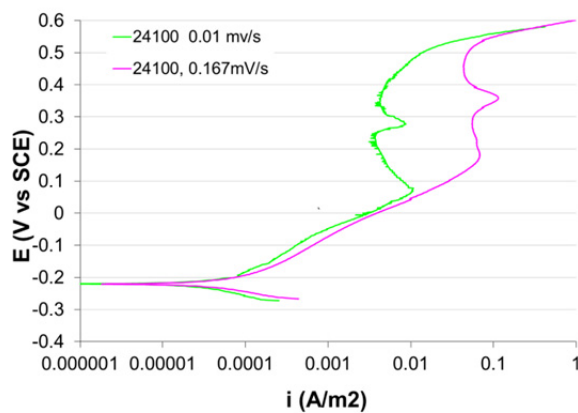


Figure 5: Cyclic polarization curves for UNS S24100 steel at scan rates of 0.01 and 0.167 mV/s

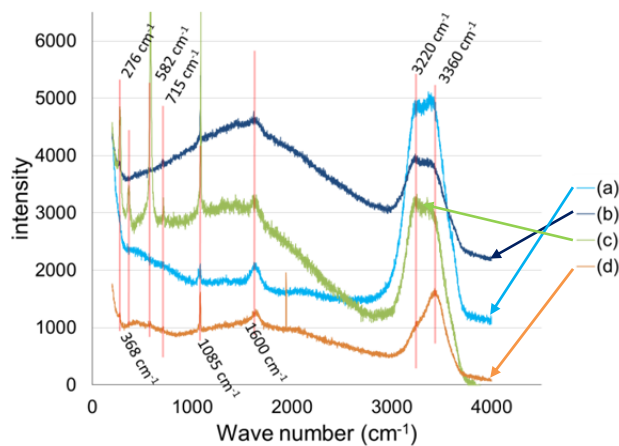


Figure 6: Raman spectra for UNS S31603 steel specimens in concrete pore solution

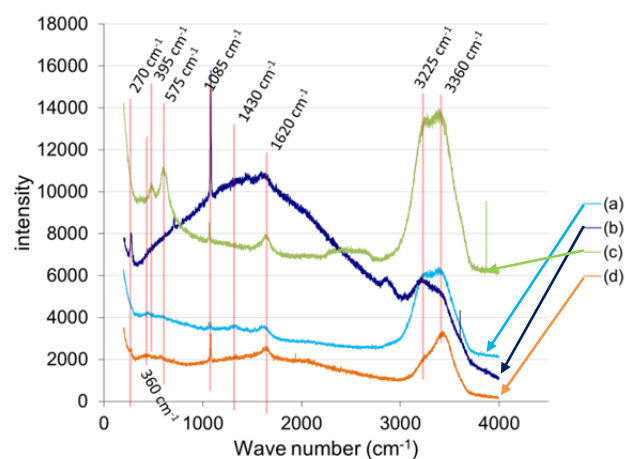


Figure 7: Raman spectra for UNS S24100 steel specimens in concrete pore solution

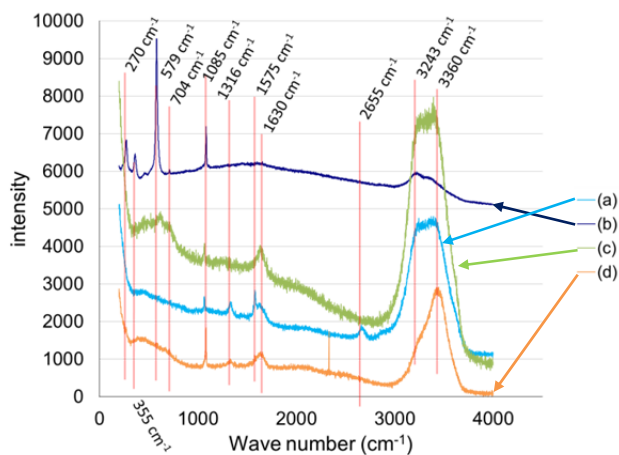


Figure 8: Raman spectra for UNS S32304 steel specimens in concrete pore solution

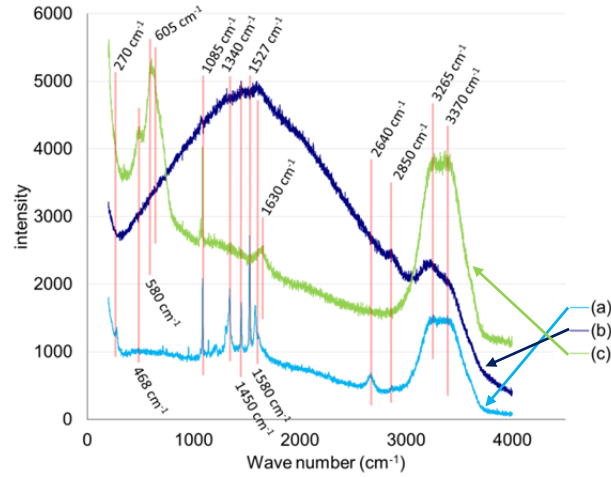


Figure 9: Raman spectra for UNS S32101 steel specimens in concrete pore solution

Numerical Study of Pore Solution Chemistry in Surface Crevices of Carbon Steel Rebar

O. Burkan Isgor, Kosta Karadakis and Pouria Ghods

Synopsis: The variability and uncertainty associated with chloride thresholds can be partly explained by the surface conditions of carbon steel rebar, in particular, by the presence of crevices on the steel surface. It has been suggested in the literature that pore solution in the crevices on the steel surface may be different from that of the bulk pore solution, and this difference may create the necessary conditions for the breakdown of the passive film. To test this hypothesis, a numerical investigation was carried out using a non-linear transient finite element algorithm, which involved the solution of coupled extended Nernst-Planck and Poisson's equations in a domain that represented typical surface crevices on carbon steel rebar. The numerical simulations showed that the chemistry of the pore solution, in particular pH and Cl^-/OH^- , within crevices provided more favourable conditions for depassivation than the bulk concrete pore solution. Local acidification and increase in Cl^-/OH^- within the crevice were observed in all simulations, albeit to different degrees. Simulations supported the hypothesis that the chemical composition of the pore solution within the crevices differs from that of the bulk solution through a process similar to the suggested mechanism of typical crevice corrosion.

Keywords: carbon steel reinforcement, corrosion, passivity, chloride, depassivation, crevice, mill scale, finite element analysis.

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INTRODUCTION

Carbon steel reinforcement in concrete is protected against corrosion by a passive film that forms in the alkaline environment of the pore solution. Chlorides may cause the loss of the passive film if their concentrations exceed threshold values, which have been reported to cover a wide range and have a high degree of uncertainty¹⁻³. The wide range and variability of chloride thresholds have been associated with the variability in the composition of the pore solutions in different types of concrete⁴⁻¹⁰, rebar-concrete interface^{11,12}, chloride binding of the hydration products of concrete¹³⁻¹⁵, oxygen availability around reinforcement^{12,16-18}, environmental conditions^{14,18}, mechanical integrity of the steel-concrete interface¹⁹ and surface characteristics of rebar^{10,17-22}.

Among these factors the effect of rebar surface characteristics to the chloride-induced depassivation of carbon steel reinforcement in concrete has been receiving increasing attention. Previous studies have shown that reduction of defects, crevices, and cracks from the rebar surface by sandblasting, polishing or pickling increases chloride thresholds by as much as one order of magnitude¹⁷⁻²⁴. Furthermore, the variability associated with chloride thresholds reduces with these surface modification processes, suggesting that as-received rebar surfaces are locally much more diverse and complex than modified surfaces^{11,24}.

In a recent microscopic study, Ghods et al.¹¹ investigated the effect of mill scale on chloride-induced depassivation of carbon steel to explain why as-received rebar is more susceptible to corrosion initiation than rebar without mill scale. Cross-sectional SEM images of rebar specimens showed that voids and crevices exist along the interface between steel and mill scale. Some of these voids and crevices were connected to the pore solution by cracks, which serve as pathways for concrete pore solution to reach the steel surface, hence allowing ion movement between the pore solution and the crevices through electrical migration and diffusion. Ghods et al.¹¹ hypothesized that over time, the chemical composition of the pore solution within the crevices begins to differ from that of the bulk solution through a process similar to the suggested mechanisms of typical crevice corrosion^{25,26}. A brief description of the mechanism proposed by Ghods et al.¹¹ is presented here as it provides a background to the present numerical investigation.

Figure 1 shows a schematic of a crevice at the interface of the steel and mill scale that is connected to the free surface by a crack. Figure 1a illustrates the conditions under which the steel is in passive state while Fig.1b shows the conditions that may lead to depassivation. During the passive stage, iron oxidizes and moves into the concrete pore solution in the crevice as a result of the anodic reaction on the steel surface:



The rate of metal loss is proportional to the passive current density because initially the steel is in the passive state. At the same time, in the presence of oxygen, the following cathodic reaction also takes place on the steel surface:



During this initial stage, the concentrations of anions and cations in the crevice are the same as those in the bulk concrete pore solution. In particular, Cl^-/OH^- , which is a measure of chloride threshold, is the same for the bulk solution and for the solution inside the crevice. As the anodic and cathodic reactions proceed, oxygen consumed by the cathodic reaction inside the crevice cannot be replenished by the diffusion-driven transport of oxygen from the bulk solution; therefore, after some time, oxygen is depleted in some crevices. In these crevices, the cathodic reaction (Eq. 2) and the local production of hydroxide slow down; however, the cathodic reaction can still take place on other parts of the steel surface that are not covered with mill scale, or even on the mill scale surface if the mill scale is sufficiently conductive; this continues to drive iron dissolution (Eq. 1) inside the crevice. Chlorides and hydroxides move into the crevice to maintain electroneutrality, but chlorides move faster, and hydroxides precipitate as $\text{Fe}(\text{OH})_2$. The result is that Cl^-/OH^- increases within the crevice relative to the bulk solution, leaving the steel exposed to the pore solution within the crevice more susceptible to depassivation than steel exposed to the bulk pore solution.

Mill scale is not the only surface characteristic of steel that may provide cracks and crevices on the rebar surface. Crevices may form on the rebar surface during the manufacturing process. Furthermore, defects and damages on epoxy-coated rebar may lead to crevices between the epoxy and the steel. Some of the elongated micro-scale pores along the steel concrete interface may also act like crevices. Therefore, the crevice-corrosion mechanism proposed by Ghods et al.¹¹ may be applicable to variety of cases. However, providing experimental evidence for such a mechanism is rather challenging due to the small scale and the transient nature of the problem. The main objective of this paper is to investigate numerically the chemistry of the concrete pore solution in the surface crevices of carbon steel rebar in order to test the hypothesis that the pore solution chemistry in these crevices may be different from that of the bulk pore solution, and this difference may create the necessary conditions for the breakdown of the passive film on the steel surface when chlorides are present.

NUMERICAL MODEL

The numerical investigation is carried out on a simplified and generic crevice on carbon steel rebar as illustrated in Fig. 2. The crevice is connected to the pore solution by a crack, which serves as pathway for concrete pore solution to reach the steel surface, hence allowing ion movement between the pore solution and the crevice through electrical migration and diffusion. It is assumed that crevice material is non-conductive, and only steel surface is the source of electrochemical reactions that take place within the crevice. This assumption is conservative in the sense that not defining any electrochemical reactions on the surfaces of the crevice material will reduce the rate of oxygen and hydroxide ion depletion within the crevice and will slow down the transport of species in the pore solution. Cases in which crevice surfaces may be partially conductive, as in the case of mill scale crevices, the changes in the pore solution chemistry within the crevice will be larger²⁷; therefore, a conservative approach is taken here to test the hypothesis that crevices that form under non-conductive surfaces may also provide critical conditions for corrosion initiation.

Governing equations

The transport of ionic, solid and gaseous species within the concrete pore solution is modelled using the extended Nernst-Planck equation²⁸:

$$\frac{\partial c_{is}}{\partial t} + \frac{\partial c_i}{\partial t} + \nabla \cdot \underbrace{-D_i \nabla c_i}_{\text{Diffusion}} - \underbrace{\frac{D_i z_i F}{RT} c_i \nabla \phi}_{\text{Electrical Migration}} - \underbrace{D_i c_i \nabla (\ln \gamma_i)}_{\text{Chemical Activity}} = 0 \quad (3)$$

where subscript i is the index representing each ionic (*i.e.*, OH^- , Fe^{2+} , Ca^{2+} , Cl^- , Na^+ , K^+), and gaseous (*i.e.*, $\text{O}_{2(g)}$) species modelled; c_i (mol/m^3 or mol/ft^3) is the concentration of species in the ionic or in the gaseous state; t (s) is time; c_{is} (mol/m^3 or mol/ft^3) is the concentration of the stationary species in solid state (*i.e.*, the components $\text{Fe}_{(s)}$ and $\text{OH}_{(s)}$ as they exist in $\text{Fe}(\text{OH})_{2(s)}$) and $\partial c_{is} / \partial t$ is the sink/source term that accounts for the exchange between the solid and ionic species in the concrete pore solution (*i.e.*, the exchange between $\text{Fe}_{(s)}$ and Fe^{+2} , and the exchange between $\text{OH}_{(s)}$ and OH^-); D_i (m^2/s or ft^2/s) is the diffusion coefficient for the species in water; R is the ideal gas constant; T (K) is the temperature; z_i is the valence of the ionic specie; F is Faraday's constant, ϕ (V) is the electric potential; and γ_i is the chemical activity coefficient for the various ionic species in water, which depends on the ionic strength of the solution. Activities in this numerical investigation were calculated iteratively using the Modified Davies Equation proposed by Samson and Marchand²⁹. The details of the iterative procedure that is used to calculate the activity coefficients are provided by Karadakis²⁷.

In Eq. 3, there are three mechanisms that are used to describe the flux of species in concrete pore solution: diffusion, electrical migration and chemical activity. Advection flux is not considered as part of the total flux of species because the analysis domain is assumed to be fully saturated with the concrete pore solution that is stationary. The diffusion term in the total flux expression represents the movement of species based on a concentration gradient. Although there is no external current applied to the system, the diffusion of ions within the pore solution creates electric potential gradients since different ions move at different velocities, and this, in turn, leads to an imbalance in the electro-neutrality of the system. These potential gradients, through the electrical migration term in Eq. 3, slow down the faster ions while accelerating the slower ions so that electro-neutrality of the system is maintained. The potential gradients change over time, and they need to be calculated for each time step during the numerical solution

of Eq. 3; therefore, in this study, Eq. 3 is coupled with the Poisson's equation that directly relates the electric potential distribution with the electric charge distribution in the concrete pore solution:

$$\nabla^2 \phi + \frac{F}{\varepsilon} \sum_{i=1}^{n_s} z_i c_i = 0 \quad (4)$$

where n_s refers to the total number of ionic species and ε is the permittivity of the medium, which is assumed in this study to be the same as water. Finally, the chemical activity term in Eq. 1 represents the ion-ion and ion-solvent interactions that take place in an ionic solution. Ion-ion interactions may reduce the mobility of certain ions in solutions due to the fact that opposite charges attract, hence an ion of a given charge moving in the solution will have oppositely charged ions attaching themselves around it. Ion-solvent interactions may also reduce the mobility of ions in a solution, but this interaction is caused by ions dragging solvent (water) molecules with them as they move in the solution.

Initial conditions, chemical reaction constraints and electroneutrality

The focus in this study is placed on the modelling of the transport of ionic, solid and gaseous species in the pore solution within the crevice while all steel surfaces in the analysis domain are assumed to be passive and experiencing microcell corrosion. The anodic and cathodic micro-cell reactions on the passive steel surface are, respectively, iron dissolution from the steel surface to the concrete pore solution (Eq. 1) and the reduction of dissolved oxygen in the pore solution (Eq. 2). The modelling of the transport of ions in the pore solution after corrosion initiation, i.e., pitting, is not within the scope of this paper.

The simulations are carried out in two simulated pore solutions named CH and CP. The label "CH" refers to a saturated calcium hydroxide, $\text{Ca}(\text{OH})_2$, solution with pH of 12.5. The solution referred as "CP" is composed of calcium hydroxide (at saturation), sodium hydroxide (NaOH) and potassium hydroxide (KOH). The CP solution (pH = 13.3) contains typical concentrations of different anions and cations that can be found in ordinary portland cement concrete pore solution.

At the beginning of the simulations it is assumed that the pore solution composition within the crevice is equal to the composition of the bulk concrete pore solution. Table 1 provides the initial composition of the concrete pore solutions when there is no chloride in the bulk solution. Dissolved oxygen concentration in both CH and CP pore solutions is assumed to be equal to 0.15 mol/m^3 (0.0043 mol/ft^3), and the concentrations of $\text{Fe}_{(s)}$ and $\text{OH}_{(s)}$ from $\text{Fe}(\text{OH})_{2(s)}$ were assumed to be 0. The initial chemical activities presented in Table 1 have been calculated using the modified Davies technique and satisfy the electroneutrality requirement.

Calcium (Ca^{2+}) and iron (Fe^{2+}) ions in the pore solution are assumed to only react with hydroxides (OH^-) to form solid calcium hydroxide and solid iron hydroxide as per Eqs. (5) and (6), respectively:



where K_{sp1} and K_{sp2} are the solubility product constants³⁰. This simplification is done because of the concern that auxiliary ions would complicate the chemistry within crevices such that it would be difficult to carry out a parametric study to investigate the effects of the variations in basic parameters such as passive current density and domain size. The stoichiometric balance among the solid species of Eqs. (5) and (6) requires that in the bulk concrete pore solution the following constraint exists:

$$c_{\text{Fe}_{(s)}} + c_{\text{Ca}_{(s)}} = 0.5 \times c_{\text{OH}_{(s)}} \quad (7)$$

The reaction rates of the reversible reactions given in Eqs. (5) and (6) can be assumed to be large in comparison to the rate of transport of species involved³¹. Accordingly, reactions given in Eqs. (5) and (6) required the following two solubility relations be satisfied simultaneously at every node in the domain³²:

$$\gamma_{\text{Ca}^{2+}} c_{\text{Ca}^{2+}} \left(\gamma_{\text{OH}^-} c_{\text{OH}^-} \right)^2 = K_{sp1} \quad (8)$$

$$\gamma_{Fe^{2+}} c_{Fe^{2+}} \left(\gamma_{OH^-} c_{OH^-} \right)^2 = K_{sp_2} \quad (9)$$

These two solubility relations must be satisfied at every node in the pore solution when their respective solid compound is present in the concrete pore solution. In addition, electroneutrality of all ionic species in the domain of analysis is strictly enforced at every step of the analysis²⁷.

Analysis domain and boundary conditions

Figure 2 illustrates the axi-symmetrical domain and boundary conditions of a typical simulation, representing a crevice on the steel surface. In the figure, boundary 1 is the opening of the crevice to the concrete pore solution; boundary 2 is the axis of symmetry; boundary 3 is the steel surface; and boundaries 4, 5 and 6 represent the surfaces of the crevice material (e.g. mill scale or epoxy) that form the crevice on the steel surface.

Boundary conditions for the extended Nernst-Planck equations — Boundary 1 represents the opening of the crack to the bulk concrete pore solution, in which concentrations of species were assumed to remain constant; therefore, for boundary 1, Dirichlet boundary conditions were defined based on the assumed concentration levels in the bulk concrete pore solution.

The boundary conditions for the steel and surfaces of the crevice material (*i.e.*, boundaries 2-6) during the solution of the extended Nernst-Planck equations were defined as Neumann conditions:

$$\mathbf{n} \cdot \mathbf{N}_i = \frac{i_{cur}}{n_e F} \quad (10)$$

where $\mathbf{n}$ is a unit vector with the direction normal to the boundary, $\mathbf{N}_i$ is the total flux of species, n_e refers to the number of electrons exchanged in the reaction, and i_{cur} (A/m² or A/ft²) is the current density, representing the rate of electrochemical reactions taking place on the boundary surfaces. Current density, i_{cur} for all species is set to zero for boundary 2, which represents the line of axi-symmetry of the analysis domain.

The steel surface (boundary 3) is assumed to be covered with a passive film; therefore, steel is in a passive corrosion state with a corrosion rate equal to the passive current density, i_p . Following Eq. (1) and (2), the boundary conditions along the steel surface should represent OH⁻ production, Fe²⁺ dissolution and O₂ depletion in the passive state; therefore, the following Neumann conditions were defined along boundary 3:

$$\mathbf{n} \cdot \mathbf{N}_{OH^-} = (i_p / F) \quad (11)$$

$$\mathbf{n} \cdot \mathbf{N}_{Fe^{2+}} = (i_p / 2F) \quad (12)$$

$$\mathbf{n} \cdot \mathbf{N}_{O_2} = -(i_p / 4F) \quad (13)$$

For all other species, i_{cur} is set to zero on boundary 3. Similarly, since it is assumed that crevice material is non-conducting, there is no electrochemical reaction on the boundaries; therefore, i_{cur} is set to zero on boundaries 4, 5 and 6.

Boundary conditions for the Poisson's equation — The solution of the Poisson's equation (Eq. 4) provides a potential gradient in the electrical migration term of the extended Nernst-Planck equation (Eq. 3). Since it is assumed that no external current was applied, for the solution of the Poisson's equation, all boundaries, except for boundary 1, are represented by the Neumann condition:

$$\mathbf{n} \cdot \nabla \phi = 0 \quad (14)$$

Boundary 1 was defined as a Dirichlet condition. Since the ultimate goal of the solution of the Poisson's equation is to solve for the potential gradient, the value of the Dirichlet condition defined on boundary 1 is not important as long

as all other boundaries are defined as “no flux” Neumann conditions; the gradients of the potentials will be the same regardless of the value of the potential used as the Dirichlet condition on boundary 1. For convenience, the Dirichlet condition on boundary 1 was defined as:

$$\phi = 0 \text{ V} \quad (15)$$

Transport properties

The diffusion coefficients of ionic species in the concrete pore solution are calculated using Einstein’s relation³⁰:

$$D_i = \frac{RTu_i}{z_i F} \quad (16)$$

As $\text{Fe}(\text{OH})_{2(s)}$ precipitates, it progressively occupies more space within the crevice; this build-up could cause a decrease in the rate of transport of species. To account for this effect, the diffusion coefficients are assumed to be related to the $\text{Fe}(\text{OH})_{2(s)}$ concentration at any given point in the analysis domain at any given time. In this model, $\text{Fe}(\text{OH})_{2(s)}$ is assumed to build up within the crevice until there is no more space left. The maximum amount of $\text{Fe}(\text{OH})_{2(s)}$ that can be found in a unit volume is $37,840 \text{ mol/m}^3$ (1071.5 mol/ft^3). When the $\text{Fe}(\text{OH})_{2(s)}$ reaches $37,840 \text{ mol/m}^3$ (1071.5 mol/ft^3) at a point in the analysis domain, the diffusion coefficients of all species in that element are assumed to be very small, typically in a range between 10^{-10} and $10^{-13} \text{ m}^2/\text{s}$ (or ft^2/s)³³. The diffusion coefficients for all other concentrations of $\text{Fe}(\text{OH})_{2(s)}$ are linearly interpolated between the maximum and minimum diffusion coefficients (*i.e.*, D_{max} and D_{min}) at $[\text{Fe}(\text{OH})_{2(s)}] = 0$ and $[\text{Fe}(\text{OH})_{2(s)}] = 37,840 \text{ mol/m}^3$ (1071.5 mol/ft^3), respectively. Table 2 provides diffusion coefficients for different species when $[\text{Fe}(\text{OH})_{2(s)}] = 0$ and $[\text{Fe}(\text{OH})_{2(s)}] = 37,840 \text{ mol/m}^3$ (1071.5 mol/ft^3).

Solution procedure

The initial-value problem defined in this paper was implemented and solved using a commercial finite element analysis software. All equations were solved using coupled transient and nonlinear solution algorithms. Because of the coupled and nonlinear nature of the problem, the computational inefficiency was a major obstacle; therefore, a comprehensive mesh study analysis was conducted to find the optimum finite element mesh that would provide a balance between computation efficiency and accuracy. The software had its own mesh generation routines and offers several alternatives for nonlinear and transient solution algorithms. All cases were discretized with Lagrangian triangular finite elements. Depending on the geometry of the analysis domain and the ionic strength of the solution the number of elements used in the analyses cases ranged from 4000 to 10,000. Additional details on the mesh study analysis, computational efficiency, and solution algorithms are provided by Karadakis²⁷. Table 3 provides a tabulated view of the constants and material properties that were used in the simulations.

ANALYSES AND RESULTS

In this paper, a typical simulation (analysis case 1) is presented in detail to demonstrate that crevices on the rebar surface, in fact, may act as local microenvironments, where the pore solution composition can differ considerably from the bulk concrete solution. Two additional cases are presented to demonstrate the effect of crevice length (analysis case 2) and the chloride concentration in the bulk solution (analysis case 3) on the composition of the pore solution within the crevice. To increase computational efficiency, these simulations were carried out for the CH solution, which provides a simpler ionic environment than the CP solution.

Analysis case 1

The first analysis presented in this section was carried out on a domain with the following dimensions: crevice crack length (l) = $5 \times 10^{-5} \text{ m}$ ($1.97 \times 10^{-3} \text{ in}$); crevice crack thickness ($t_l/2$) = $5 \times 10^{-8} \text{ m}$ ($1.97 \times 10^{-6} \text{ in}$); crevice length ($c/2$) = $1.5 \times 10^{-3} \text{ m}$ ($5.9 \times 10^{-2} \text{ in}$); crevice thickness (t_c) = $1 \times 10^{-6} \text{ m}$ ($3.9 \times 10^{-5} \text{ in}$). The simulations were carried out in the CP solution; the chloride concentration in the bulk CP solution was 1250 mol/m^3 (35.4 mol/ft^3). A constant passive current density, i_p , of $2 \times 10^{-3} \text{ A/m}^2$ ($1.3 \times 10^{-6} \text{ A/in}^2$) was applied on steel surfaces. Diffusion coefficients of species were assumed to linearly decrease from D_{max} to D_{min} , as per Table 2.

The activities of the ionic species and the concentration of the gaseous species (*i.e.*, O_2) are presented along the crevice crack (boundary 2) and along the steel surface (boundary 3) after steady-state conditions are reached ($t = 10^9$

s) in Fig. 3. In Figure 3a, the activity of hydroxide is shown to be decreasing towards the tip of the crevice (point A). In Figure 3b, the activity of chloride is shown to be increasing towards the tip of the crevice (point A). The steady-state profiles of other ions (i.e., Ca^{+2} , Fe^{+2} , Na^{+} and K^{+}) and oxygen concentration are also presented in Fig. 3.

In order to explain these trends, changes in the activities of hydroxide and chloride, and the change in oxygen concentration, over time are plotted at the tip of the crevice (i.e., point A), in Figures 4a and 4b, respectively. Anodic reactions produce Fe^{+2} ions on the steel surface (hence the increase in the activity of Fe^{+2} observed in Figure 3a), and cathodic reactions consume oxygen from the pore solution and produces hydroxide near the steel surface. When anodic and cathodic reactions are in balance, the expected outcome is an increase in the activity of hydroxide; however, as shown in Figure 4a, an opposite pattern is observed. It can be seen in Figure 4b that, after a short period during which anodic and cathodic reactions at point A are in balance, the oxygen concentration at point A starts decreasing sharply from its initial condition of 0.15 mol/m^3 (0.0043 mol/ft^3) to zero. The decrease is mainly due to the oxygen consumption by the cathodic reactions on the steel surface, but accelerated due to the slow diffusion of oxygen from the bulk solution towards the tip of the crevice (point A): the consumed oxygen is not replenished by the oxygen diffusing from the bulk solution. When the oxygen is completely consumed at point A, the cathodic reaction cannot continue there, but the anodic reaction still takes place since electrons produced in the anodic reaction can still be consumed in cathodic reactions on other parts of the steel where the pore solution still contains oxygen. The termination of the cathodic reaction at point A results in the termination of hydroxide production there; therefore, the hydroxide activity starts to decrease at point A because the Fe^{+2} ions produced in the anodic reaction reacts with hydroxides to produce $\text{Fe}(\text{OH})_{2(s)}$. Eventually, continued production of Fe^{+2} ions and decreased amounts of hydroxide causes an imbalance in the electroneutrality in the pore solution near point A such that total positive charge becomes larger than total negative charge. This imbalance in electroneutrality creates a strong electrochemical gradient between the pore solution near point A and the bulk pore solution, which contains large amounts of negatively charged ions such as hydroxides and chlorides; therefore hydroxides and chlorides start moving towards the tip of the crevice (point A) where they are needed to establish electroneutrality.

As it can be seen in Table 2, the mobility of chlorides are smaller than that of hydroxides by a factor of ~ 3 ; however, the chloride activity near point A starts increasing sharply, while hydroxide activity decreases, as shown in Figure 3.3a, because hydroxides are continuously consumed to produce $\text{Fe}(\text{OH})_{2(s)}$ in the pore solution. The tip of the crevice was selected for the description above since it is the farthest point within the crevice from the bulk pore solution. However, the same mechanism occurs at other parts of the crevice; therefore when steady-state conditions are reached, the profiles given in Fig. 3 can be plotted along the crevice crack and crevice boundaries. The result is an increase in the chlorides and a decrease in the hydroxides within the crevice as illustrated in Fig. 5.

Analysis case 2

In this scenario, the effect of crevice length on the composition of the pore solution within the crevice was investigated. The geometry of the crevice crack and crevice was mostly fixed such that crack length (l) was $5 \times 10^{-5} \text{ m}$ ($1.97 \times 10^{-3} \text{ in}$), crevice crack thickness ($t/2$) was $5 \times 10^{-8} \text{ m}$ ($1.97 \times 10^{-6} \text{ in}$), and crevice thickness (t_c) was $1 \times 10^{-6} \text{ m}$ ($3.9 \times 10^{-5} \text{ in}$). The analyses were carried out for different crevice lengths ($c/2$) of $5 \times 10^{-4} \text{ m}$ ($1.97 \times 10^{-2} \text{ in}$), $7.5 \times 10^{-4} \text{ m}$ ($2.95 \times 10^{-2} \text{ in}$) and $1 \times 10^{-3} \text{ m}$ ($3.9 \times 10^{-2} \text{ in}$). Passive current density was assumed to follow a variable pattern such that it was constant at $2 \times 10^{-3} \text{ A/m}^2$ ($1.3 \times 10^{-6} \text{ A/in}^2$) until $\text{Cl}^-/\text{OH}^- = 3$, then it increased linearly to $3.4 \times 10^{-2} \text{ A/m}^2$ ($2.19 \times 10^{-5} \text{ A/in}^2$) until $\text{Cl}^-/\text{OH}^- = 5$ and remained constant at this value. Such a variable pattern of passive current density as a function of Cl^-/OH^- has been widely observed in the literature. The chloride concentration in the bulk CH solution was 500 mol/m^3 (14.15 mol/ft^3). A lower chloride exposure concentration was chosen for the analysis in the CH solution because of the lower pH of the CH solution ($\text{pH} = 12.5$) compared to that of the CP solution ($\text{pH} = 13.3$). Diffusion coefficients of species were assumed to linearly decrease from $D_{\max}$ to $D_{\min}$, as per Table 2.

The pH and Cl^-/OH^- along the crevice crack (boundary 2) and steel surface (boundary 3) for the CH solution are shown in Fig. 6. In this figure, the results of three crevice lengths are presented for a bulk pore solution with a pH of 12.43 and Cl^-/OH^- of 12.64. For the analysis of the $5 \times 10^{-4} \text{ m}$ ($1.97 \times 10^{-2} \text{ in}$) crevice length (Fig. 6a), Cl^-/OH^- is shown to increase to 33.85 at the tip of the crevice (point A), but the pH drops only to 12.01 at steady-state conditions (i.e., $t = 10^9 \text{ s}$). For larger crevice lengths (Figs. 6b and 6c), Cl^-/OH^- at the tip of the crevice increases by 3 orders of magnitude while the pH drops below 10, indicating local acidification within the crevice. These conditions are likely to cause depassivation of steel within the crevice. Comparison of the analysis cases 1 and 2, respectively carried out

for CP and CH solutions, show that for similar crevice dimensions the pore solution composition within the crevice experience quite different ranges of acidification (pH decrease) and Cl^-/OH^- increase.

It should also be noted that all crevices do not create the conditions for depassivation. Geometry of the crevice has a significant impact on whether a crevice will provide adequate local acidification (reduction in pH) and increase in Cl^-/OH^- ratio. When the crevice thickness is large (e.g. t_c greater than 1×10^{-4} m or 3.9×10^{-3} in) such that O_2 in the crevice cannot be fully consumed by the cathodic microcell reaction that takes place on steel surface, crevice corrosion mechanism described in this paper does not take place. Similarly if the crevice length is too small (e.g. l smaller than 1×10^{-5} m or 3.9×10^{-4} in), O_2 in the crevice can be replenished quickly from the bulk solution; therefore, the crevice corrosion mechanism is not observed.

Analysis case 3

The effect of the chloride amount in the bulk concrete pore solution on the composition of the pore solution within the crevice was studied in this case. The geometry of the crevice was as follows: crack length (l) = 5×10^{-5} m (1.97×10^{-3} in), crevice crack thickness ($t/2$) = 5×10^{-8} m (1.97×10^{-6} in), and crevice thickness (t_c) = 1×10^{-6} m (3.9×10^{-5} in) and crevice lengths ($c/2$) = 5×10^{-4} m (1.97×10^{-2} in). Passive current density was assumed to follow a variable pattern. It was constant at 2×10^{-3} A/m² (1.3×10^{-6} A/in²) until $\text{Cl}^-/\text{OH}^- = 3$, then it increased linearly to 3.4×10^{-2} A/m² (2.19×10^{-5} A/in²) until $\text{Cl}^-/\text{OH}^- = 5$ and remained constant at this value. Three bulk chloride concentrations of 500 mol/m³ (14.15 mol/ft³), 100 mol/m³ (2.83 mol/ft³), and 50 mol/m³ (1.41 mol/ft³) were analyzed in this case. Diffusion coefficients of species were assumed to linearly decrease from $D_{\max}$ to $D_{\min}$, as per Table 2.

Figure 7 shows the pH and Cl^-/OH^- along the crack length (boundary 2) and crevice length (boundary 3) at three chloride concentrations in the bulk CH pore solution. It can be observed that the case with the lowest chloride concentration in the bulk solution did not have any major effect on pH or Cl^-/OH^- . However, the two cases with larger chloride concentrations in the bulk solution caused pH to drop below 10 and Cl^-/OH^- to increase above 3 at the tip of the crevice (point A). The results of these two simulations are shown to be nearly equivalent to each other in Fig. 7, but the times at which the plots were made were different: the case with a chloride level of 100 mol/m³ (2.83 mol/ft³) reached a pH of ~ 9.5 at a time of 1.1×10^7 s, while the case with a chloride level of 50 mol/m³ (1.41 mol/ft³) reached a pH of ~ 9.5 at a time of 2.3×10^7 s. It is clear from these simulations that chloride concentration in the bulk solution is a critical parameter affecting the chemistry of the pore solution with crevices. If the chloride concentration in the bulk solution is low, steel surfaces in the crevice may remain passive. The concentration of chloride in the bulk solution affects when depassivation conditions will be reached within the crevice.

CONCLUSIONS

The numerical simulations showed that the pore solution composition in the crevices that exist on rebar surface is different from that of the bulk pore solution: local acidification (*i.e.*, a drop in pH) and increase in Cl^-/OH^- were observed in all simulations, albeit to different degrees. The largest drop in pH and the largest increase in Cl^-/OH^- occurred at the tip of the crevice, which was the farthest point of the crevice from the bulk solution. The changes in pH and Cl^-/OH^- increased with increasing length of the crevice, indicating a relationship between crevice geometry and the composition of the pore solution within the crevice. It was also shown that the amount of chloride in the bulk concrete pore solution affects the local composition of the pore solution (*i.e.*, pH and Cl^-/OH^-) in the crevice. Simulations supported the hypothesis proposed by Ghods et al.¹¹ such that the chemical composition of the pore solution within the crevices differ from that of the bulk solution through a process similar to the suggested mechanism of typical crevice corrosion.

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Table 1 — Initial activities of species in the CH and CP solutions before chloride addition

Activity, $c_i\gamma_i$						
Solution	Cl⁻	OH⁻	Fe²⁺	Ca²⁺	Na⁺	K⁺
CH	0	25.96	0	8.16	0	0
CP	0	218.20	0	0.12	74.06	141.96

Table 2 — Transport properties of all species in the concrete pore solution

Species	Mobility ³⁴ , $u_i \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ($\times 10^{-5} \text{ in}^2 \text{ s}^{-1} \text{ V}^{-1}$)	Diffusion coefficient, $D_{\max_i}$, m^2/s when $c_{\text{Fe(s)}} = 0$ (ft^2/s)	Diffusion coefficient, $D_{\min_i}$, m^2/s when $c_{\text{Fe(s)}} = 37,840$ mol/m^3 (1071.5 mol/ft^3) (ft^2/s)
OH⁻	20.56 (31.87)	5.28×10^{-9} (5.68×10^{-8})	5.28×10^{-13} (5.68×10^{-13})
Fe²⁺	5.60 (8.68)	0.72×10^{-9} (7.75×10^{-9})	0.72×10^{-13} (7.75×10^{-14})
Ca²⁺	6.17 (9.56)	0.79×10^{-9} (8.50×10^{-9})	0.79×10^{-13} (8.50×10^{-14})
Cl⁻	7.92 (12.28)	2.03×10^{-9} (2.19×10^{-8})	2.03×10^{-13} (2.19×10^{-13})
Na⁺	5.19 (8.04)	1.33×10^{-9} (1.43×10^{-8})	1.33×10^{-13} (1.43×10^{-13})
K⁺	7.62 (11.81)	1.96×10^{-9} (2.11×10^{-8})	1.96×10^{-13} (2.11×10^{-13})
O₂³⁵	-	2.20×10^{-9} (2.37×10^{-8})	2.20×10^{-13} (2.37×10^{-13})

Table 3 — Constants and analysis parameters used in the numerical model

Parameter	Value	Description
T	298 K	Temperature
R	8.3143 J/mol/K	Ideal gas constant
F	96488 C/mol	Faraday's constant
K_{sp1}	5500 mol ³ /m ⁹	Solubility product constant of Ca(OH) _{2(s)} ³⁰
K_{sp2}	4.87x10 ⁻⁸ mol ³ /m ⁹	Solubility product constant of Fe(OH) _{2(s)} ³⁰
ϵ_0	8.854x10 ⁻¹² C ² /N/m ²	Permittivity of the vacuum ²⁹
ϵ_r	80.1	Dielectric constant of water ²⁹
ϵ	7.092x10 ⁻¹⁰ C ² /N/m ²	Permittivity of the medium ²⁹