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IMPACT ON ANTICIPATED SERVICE LIFE OF CHLORIDE THRESHOLDS

Kyle Stanish

Synopsis: The corrosion-initiation threshold for corrosion is a key parameter that controls the expected service life of a concrete structure. Different methods of establishing threshold values that consider different components of concrete mixtures can have a significant impact on anticipated service life. This impact is evaluated using typical concrete mixtures that are used in structures exposed to chloride-laden environments across the United States. The often synergistic impact of including supplementary cementing materials (SCMs) in a concrete mixture and corrosion-initiation thresholds is examined, where the reduction of diffusion values with time can lead to a greater impact that would be expected from variation in corrosion-initiation thresholds alone.

Keywords: Concrete; Corrosion; Service Life Modelling; Corrosion-Initiation Thresholds; Supplementary Cementitious Materials

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Kyle Stanish, Ph.D., S.E., P.E., ACI member, is a Senior Restoration Consultant at Walker Restoration Consultants in Chicago, IL. He completed his Ph.D. in 2002 at the University of Toronto, Toronto, Canada on the migration of chloride ions in concrete under an electrical potential gradient. He currently evaluates deteriorated concrete structures and designs appropriate rehabilitation approaches. He is currently the Secretary of ACI 365: Service Life Prediction.

INTRODUCTION

The service life of a concrete structure is determined by a number of mechanisms, but chloride-induced corrosion frequently controls for concrete structures exposed to either deicing salts or salt water. For a conventionally reinforced concrete structure, the time to first repair depends on the rate at which chlorides enter the concrete (the diffusion coefficient), the depth of the surface steel layer and the corrosion-initiation threshold.

Supplementary cementing materials (SCMs) have become ubiquitous in concrete mixtures. While this is a 'green' exercise as it diverts materials from disposal, it also improves the properties of the concrete mixture. Among other effects, the use of SCMs has been shown to reduce the long term diffusion coefficients of concrete. The current ACI building code for concrete [ACI 318-14] bases chloride limits solely on the Portland cement content of the mixture, however. Inclusion of large proportions of SCMs can have the effect of reducing the corrosion-initiation threshold when expressed in terms of the mass of the concrete. The impact that this has on the expected service life of a concrete exposed to a chloride-laden environment is discussed.

BACKGROUND

In reinforced concrete structures, the steel embedded in the concrete is initially passivated. In the high pH environment that is present in the concrete pores, a thin dense oxide layer is formed which is tightly adhered to the steel. This tightly adhered layer then prevents further corrosion of the reinforcing steel. Until this layer is compromised, the steel remains protected.

The expected service life of a concrete structure exposed to a chloride-contaminated environment is usually controlled by the onset of corrosion. Corrosion of the reinforcing steel is initiated by chloride ions penetrating through the concrete and reaching to the level of the steel. When sufficient concentration of chloride ions is reached, the protection provided by the passivating layer is overcome, and corrosion will initiate. The chloride concentration that is necessary for corrosion to initiate is referred to as the corrosion-initiation threshold.

The corrosion-initiation threshold has been studied extensively [ACI 222; Virmani, 2012; Mohammed and Hamada, 2006; Pradham, 2007, among others], and there has been a wide scatter in the reported results [Angst, 2011]. The concentration value varies depending upon a number of factors, including whether it is acid-soluble or water-soluble chlorides, if the chlorides are admixed or are entering mature concrete, the composition of the concrete and the moisture content of the concrete, among other factors. Typical values range from 0.2 % to 0.4 % by mass of cement.

The amount of time it takes for chloride to reach the corrosion-initiation threshold is a significant portion of the expected service life of the concrete structure. The time after corrosion initiates until damage occurs is relatively short for conventional reinforcing steel in the typical conditions it is used. To predict the time to corrosion, there are a number of service life modelling programs available [ACI 365; Ehlen et al., 2009; Samson and Marchand, 2007; Concrete Society, 2004; Scheissl et al., 2004 among others]. They are all typically based on non-steady state diffusion of chloride ions through the concrete pore structure as modelled by Fick's Second Law:

$$\frac{dC}{dt} = -D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

Different models can vary in how they account for variations in concrete properties with time, whether they explicitly or implicitly account for chloride binding, or if they use extended versions of the basic equation that accounts for charge separations and ion-ion interaction. The service life model selected for a specific project will depend upon the project objectives.

For the purposes of this study, the service life modelling program used was Life-365 [Ehlen et al, 2009]. Life-365 is a freely available program that was developed under the auspices of an industry consortium. This study could be performed with different service life programs, but the trend of the results would be similar. Diffusion is modelled in Life-365 by a finite element application of Fick's Second Law, using effective diffusion coefficient values that implicitly include the influence of chloride binding. The development of diffusion coefficients with time is accounted for by the equation:

$$D(t) = D_{28} \left(\frac{28}{t}\right)^m$$
(2)

where D(t) is the diffusion coefficient as a function of time, D_{28} is the diffusion value at 28 days, t is the time in days and m is a parameter that depends on the cementitious materials used in the concrete.

This approach follows the work of a number of researchers [Bamforth, 1998; Thomas and Bamforth, 1999; Tang and Nilsson, 1992; Mangat and Molloy, 1994; Maage et al, 1995]. Suggested values of these parameters are provided by the program, but they can be adjusted by the user. External temperature history and surface concentrations are also provided by the program for different locations.

Once the chloride concentration reaches the corrosion-initiation threshold, the program considers that corrosion has begun, but this is not considered the end of the service life of the concrete structure. There is also a propagation period considered, during which damage to the steel bars due to corrosion is occurring but the damage has not reached sufficient magnitude to be visible or to require repair. The duration of this period varies depending upon the type of steel used (black or epoxy coated) but is modelled by Life-365 as fixed duration independent of the concrete mixture. For the purposes of this study, black steel was considered and the standard propagation period of 6 years suggested by the program was used. The combination of the time-to-initiation and the propagation period is the time to first repair and is the parameter of interest. Although Life-365 does model the remaining life of the structure after the predicted time to first repair, this was not considered in this study.

Chloride Concentration Units

There are three common units that chloride concentrations, and corrosion-initiation threshold values are typically expressed: (i) as the ratio of chloride concentration to hydroxide concentration in the pore solution ([Cl⁻]/[OH⁻]), (ii) as the percentage by mass of cement content, or (iii) as percentage by mass of concrete.

The chloride:hydroxide ratio is frequently used in laboratory studies, where the concentration in the pore solution around the bar of these two species can be directly measured. The corrosion-initiation threshold occurs when the steel depassivates and its protective oxide layer is compromised [Broomfield, 1997]. In the presence of chlorides, a simple model of depassivation is that the competition between chloride ions forming FeCl₂ and hydroxide ions forming Fe(OH)₂ favors the production of ferrous chloride. Thus the relative concentration of these two ions is the parameter of interest, although, as with all things that have to do with concrete, it is in reality more complicated than that simple model. Although this has been successful in laboratory studies of corrosion-initiation threshold [ACI 222R-01; CEB, 1992], it is difficult to implement in practice. Predicting the hydroxide concentration at the level of the steel is not a simple exercise, depends on a number of unknown parameters, and can vary with time. It is particularly difficult during the schematic design phase of the structure prior to it being built.

As an alternative to using the chloride:hydroxide ratio for expressing chloride concentrations, the chloride as the mass percent of the cement in the concrete is often used. The cement content becomes a proxy for the hydroxide concentration as the majority of hydroxide in the concrete pore solution originates from the cement and is liberated during the cementing reactions [Neville, 2002]. The cement contents is easily determined from the concrete mix designs, if they are known. This is the approach that is used in the ACI building code [318-14]. This approach is straight-forward to implement when the source of chlorides are internal, that is they come from the concrete mixture components. It does have some limitations when the source of chlorides is external to the concrete, and they are penetrating by diffusion, permeation, sorption or some other transport mechanism.

The final alternative is expressing the chloride concentration in terms of the mass percent of the concrete. This has the advantage of being able to be directly measured for existing structures. It is also how concrete experiences chlorides penetrating from the outside. Chloride-contaminated water penetrates the pore structure over the entire

surface, and is thus related to the concrete as a whole, and not the cement content alone, although it will be affected by the porosity of the concrete. It is believed that this measurement technique is more directly applicable for an external source of chlorides, and it what is frequently used in service life modelling to characterize the external environment.

SERVICE LIFE MODELLING

To evaluate the impact of corrosion-initiation threshold on predicted life, two typical structures that are exposed to chloride ions were considered. In order to capture the two extremes of behavior within the continental United States, two models were run as the base line. To represent cold weather climates with heavy use of deicing salts, a parking structure in Chicago, Illinois was considered. To represent a warm climate exposed to salt water, a jetty or pier in Miami, Florida was also evaluated. The effective diffusion coefficient is dependent on the temperature, accelerating at higher temperature. This is modelled in Life-365 using an Arrhenius relationship, with an activation energy of 3500 J/mol [Ehlen et al, 2009]. The environmental exposure conditions for these two locations, as recommended by Life-365, are shown in Table 1. These consist of the average monthly temperature (based on historic records) and the chloride surface concentration by mass of concrete. The chloride surface concentration is assumed to start at 0 % and build linearly to some maximum over a number of years. Both the maximum chloride surface concentration and the number of years it takes to reach that maximum vary depending on location and structure type. Both structures were modelled with a 2 in. (50 mm) cover over the reinforcing steel.

	Annual Temperature Profile [°F (°C)]						Surface	[Cl ⁻]						
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Max	Time
Chicago	21	25	37	49	59	69	73	72	64	53	40	27	1.0 %	7.1 yrs
	(-6)	(-4)	(3)	(9)	(15)	(20)	(23)	(22)	(18)	(12)	(4)	(-3)		
Miami	67	69	72	75	79	81	83	83	82	78	74	69	1.0 %	10 yrs
	(20)	(20)	(22)	(24)	(26)	(27)	(28)	(28)	(28)	(26)	(23)	(21)		

Table 1 – Environmental Conditions

In accordance with ACI 318-14, the corrosion-initiation threshold concentration is considered to be dependent on the amount of cement in the concrete mixture. For a concrete with 760 lb/vd^3 (450 kg/m³) of cement and a density of 3800 lb/yd³ (2255 kg/m³), a chloride concentration of 0.4 % by mass of cement translates into a threshold value of 0.08 % by mass of concrete, while 0.2 % by mass of cement is 0.04% by mass of concrete.

Influence of Corrosion-Initiation Threshold Concentration on Portland Cement Concrete

The impact of the corrosion-initiation threshold concentration is shown for a typical concrete that is made with 100 % Portland cement and no supplementary cementing materials is shown in Figure 1. This is based on a concrete with a w/cm ratio of 0.40. The diffusion parameters predicted by Life-365 for this concrete are a $D_{28} = 1.23 \times 10^{-8} \text{ in.}^{2}/\text{s}$ $(7.94 \text{ x } 10^{-12} \text{ m}^2/\text{s})$ and an m-value of 0.20.



Threshold	Chicago	Miami
0.08 % (conc)	13.3 yr	14.2 yr
0.06 % (conc)	12.5 yr	13.2 yr
0.05 % (conc)	12.0 yr	12.6 yr
0.04 % (conc)	11.5 yr	12.0 yr

Niami 🕅

Figure 1 – Effect of Threshold Concentration on Time to First Repair, Typical Portland Cement Concrete.

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Influence of Corrosion-Initiation Threshold Concentration on a Fly Ash-containing Concrete

The impact of the corrosion-initiation threshold concentration is shown for a concrete that contains fly ash is shown in Figure 2. This is based on a concrete with a w/cm ratio of 0.35 and a fly ash content of 25 %. The diffusion parameters predicted by Life-365 for this concrete are a $D_{28} = 1.10 \times 10^{-8} \text{ in.}^{2}/\text{s}$ (7.10 x 10⁻¹² m²/s) and an m-value of 0.40.



Threshold	Chicago	Miami
0.08 % (conc)	21.9 yr	23.1 yr
0.06 % (conc)	19.7 yr	20.8 yr
0.05 % (conc)	18.5 yr	19.5 yr
0.04 % (conc)	17.2 yr	18.2 yr

Figure 2 – Effect of Threshold Concentration on Time to First Repair, Fly Ash-containing concrete.

Influence of Corrosion-Initiation Threshold Concentration on a Slag-containing Concrete

The impact of the corrosion-initiation threshold concentration is shown for a typical concrete that contains slag is shown in Figure 3. This is based on a concrete with a w/cm ratio of 0.35 and a slag content of 50 %. The diffusion parameters predicted by Life-365 for this concrete are a $D_{28} = 9.34 \times 10^{-9}$ in.²/s (6.02 x 10⁻¹² m²/s) and an m-value of 0.49.



Threshold	Chicago	Miami
0.08 % (conc)	37.5 yr	38.0 yr
0.06 % (conc)	32.2 yr	32.9 yr
0.05 % (conc)	29.4 yr	30.3 yr
0.04 % (conc)	26.7 yr	27.6 yr

⊗ Miami

Figure 3 – Effect of Threshold Concentration on Time to First Repair, Slag-Containing Concrete.

DISCUSSION

The corrosion-initiation threshold concentration did affect the predicted time to first repair for all of the concrete mixtures studied for both locations. Figure 4 and 5 display the time to first repair normalized by value for a threshold concentration of 0.04 % by mass of concrete for both the Chicago and Miami structures. The impact of the threshold concentration on time to first repair does not have a direct one-to-one correlation. Doubling the threshold concentration did not double the time to first repair. This is due to the non-linear nature of diffusion, particularly at the relatively low concentrations (compared to the surface concentration) that are of interest. There is a large portion of the time between first exposure and the time the threshold concentration is reached that there are no chlorides at the level of the steel. This time does not vary when different threshold values are considered.



Figure 4 – Normalized Time to First Repair – Chicago.



The impact of varying the threshold concentrations was more significant for the mixtures containing supplementary cementing materials than for when there are no supplementary cementing materials, as can be seen in Figures 4 and 5. This increased relative impact of the corrosion-initiation threshold concentration for the modelled concrete mixtures is due to the evolution of the diffusion value with time. With the concrete mixtures containing supplementary cementing materials, the time required for the chloride concentration to reach the threshold value is longer. This provides more time for the diffusion value to reduce, which has a synergistic effect. Supplementary cementing materials have a larger m-value, or the rate at which the diffusion coefficient reduces with time than concrete mixture containing only Portland cement. [Tang and Nilsson 1992; Mangat and Molly, 1994; Maage et al, 1995; Bamforth 1998; Thomas and Bamforth, 1999; Stanish and Thomas, 2003] Thus variations in assumed threshold concentrations have a greater impact on the time to first repair for concretes containing fly ash or slag than they would with a plain Portland cement mixture.

The appropriate threshold value for different concrete mixtures will vary, however. According to ACI 318 [2014], the corrosion-initiation threshold concentration is depending only upon the cement content of the concrete mixture. When a portion of the cement is replaced by supplementary cementing materials, the amount of chloride that is permitted to be in the concrete as a whole is reduced. The use of 25 % fly ash, for example, would reduce the threshold concentration by mass of concrete by 25 % as compared to an identical concrete mixture that is only contains Portland cement. Supplementary cementing materials are not an inert substance. They do react and influence the composition of the pore solution, and thus affect the corrosion-initiation threshold concentration [Fagerlund, 2011]. However, the influence that they have will not be the same as if they were an inert, non-reacting material. Their contribution will likely be different that the contribution of Portland cement and will likely vary between different supplementary cementing materials. Determining the appropriate influence is important for predicting the expected time to first corrosion of a concrete mixture. This is particularly important for concrete that has a long expected service life as is typically the case when supplementary cementing materials are used.

CONCLUSIONS

The time to first repair for two different structures that would be typically exposed to chlorides were modelled with three different typical concrete mixtures, varying the corrosion-initiation threshold using a freely available service life program, Life-365. Based upon this investigation, it could be seen that:

- 1. The time to first repair does not have a one-to-one correlation with the assumed chloride-initiation threshold value. Doubling the corrosion-initiation threshold value does not double the time to first repair.
- 2. The variation of the time to first repair with chloride initiation threshold values is more significant for concrete that has a longer expected service life. This is attributable to the greater decrease in chloride diffusion value that occurs with longer time spans of interest.
- 3. The synergistic effect of longer time spans allowing reduced chloride diffusion coefficients is more pronounced when the concrete mixture contains supplementary cementing materials such as fly ash and slag. This is due to their greater rate of reduction of diffusion coefficient with time as compared to a Portland cement mixture.

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THE INFLUENCE OF SCM TYPE AND QUANTITY ON THE CRITICAL CHLORIDE CORROSION THRESHOLD

David Trejo and Cody Tibbits

Synopsis: Chloride-induced corrosion of embedded metals in reinforced concrete structures is dependent on the quantity of chlorides in the concrete material. Because of this, most ACI documents limit the amount of chlorides in the concrete for new reinforced concrete structures. Most documents in the United States limit the chlorides as a function of cement content, generally accepted to be the portland cement content. Significant changes have occurred in the cement and concrete industries, such as performance based specifications for cement (e.g. ASTM C1157) and the ubiquitous use of SCMs. The allowable chloride limits published by ACI Committee 222 specifically states that the allowable limits are based on portland cement content. ACI 318 specifies limits based on weight of cement but is not clear on what determines cement (portland cement only or all cementitious materials?). At issue is whether the allowable chloride limits reported by ACI and other organizations are applicable for mixtures containing SCMs and whether these limits should be based on portland cement content or total cementitious materials (cement + SCM) content. Significant research has been performed to assess the influence of SCMs on transport properties but limited research has been performed on assessing the influence of SCMs on the critical chloride corrosion threshold of steel in concrete. This paper reports on research investigating the influence of SCMs replacement types and quantities on the diffusivity and critical chloride corrosion threshold. Mortar mixtures containing fly ash had three levels of fly ash (0, 20, and 40%) and mortar mixtures containing slag had three levels of slag (0, 30, and 60%). The reinforcing steel for all specimens was conventional steel reinforcement meeting ASTM A615 specifications. Results indicate that the diffusivity of the mixtures containing SCMs was significantly lower than the mixture with portland cement as the only binder. The results also indicate that the critical chloride threshold levels for mixtures

portland cement as the only binder. The results also indicate that the critical chloride threshold levels for mixtures containing SCMs is significantly lower than the critical chloride threshold of mixtures containing only portland cement as the binder. An analysis of time to corrosion indicates that although the mean time to corrosion can be lower for systems containing SCMs, t-tests indicate that the null hypothesis (that the means of the time to corrosion of the systems are equal) cannot be rejected. This indicates that although there is a significant reduction (positive influence) in diffusivity when using SCMs, there is also a significant reduction (negative influence) in critical chloride threshold. The benefits of the reduction in the rate of diffusivity seems to be offset by the detrimental effects of SCMs on critical chloride threshold. Limits on allowable chlorides in concrete for new construction published by ACI 222 were based on concretes containing only portland cement as the binder. This research indicates that the ACI published limits may not be applicable to systems containing SCMs and that the limits are less conservative when basing the limits on total cementitious materials content.

Keywords: Corrosion; Chloride transport; Diffusion coefficient; Diffusivity; Critical chloride corrosion threshold; Chloride; Fly ash; Slag; Portland cement