



The Effects of Cement Alkalinity upon the Pore Water Alkalinity and the Chloride Threshold Level of Reinforcing Steel in Concrete

Jingak Nam¹⁾, William H. Hartt¹⁾, and Kijoon Kim^{2)*}

¹⁾ Florida Atlantic University, Florida, USA

²⁾ Korea Maritime University, Busan, Korea

(Received November 26, 2003; Accepted March 15, 2004)

Abstract

Cement of three alkalinities (equivalent alkalinities of 0.36, 0.52 and 0.97) was employed in fabricating a set of classical G109 type specimens. To-date, these have been subjected to a one week wet-one week dry cyclic ponding using 15 w/o NaCl solution. At the end of the dry period, potential and macro-cell current were measured to indicate whether the top reinforcing steel was in the passive or active state. Once this bar became active, the specimen was autopsied and the extent of corrosion was documented. Subsequent to visual inspection, concrete powder samples were collected from the upper region of the top rebar trace; and at a certain times concrete cores were taken from non-reinforced specimens. Using these, determinations were made of (1) critical chloride concentration for corrosion initiation (Cl_{th}^-), (2) effective chloride diffusion coefficient (D_e), and (3) pore water alkalinity ($[OH^-]$).

The pore water alkalinity was strongly related to the alkali content of cement that was used in the mix. The chloride concentration, $[Cl^-]$, was greater at active than at passive sites, presumably as a consequence of electro migration and accumulation of these species at active site subsequent to corrosion initiation. Accordingly, $[Cl^-]$ at passive sites was considered indicative of the threshold concentration for corrosion initiation. The Cl_{th}^- was increased with increasing Time-to-corrosion (T_i). Consequently, the HA(High Alkalinity) specimens exhibited the highest Cl_{th}^- and the NA(Normal Alkalinity) was the least. This range exceeds what has previously been reported in North America. In addition, the effective diffusion coefficient, D_e , was about 40 percent lower for concrete prepared with the HA cement compared to the NA and LA(Low Alkalinity) ones.

Keywords: concrete, cement alkalinity, reinforcing steel, corrosion, chloride threshold concentration, air voids

1. Introduction

The nature of the electrolyte is a dominant factor in corrosion processes, including that for steel in concrete, where hydroxide serves as a passivator and chloride as an activator. Thus, the onset of reinforcing steel corrosion in concrete is mainly determined by the competing influence of these two species. The pH of concrete pore solution is typically in the range 13~13.5 as a consequence of alkali from the cement, the concentration of which is normally less than one percent.¹⁾ This pH is also affected by the cement content of the mix and by exposure conditions.²⁾ The high alkalinity of pore water provides corrosion protection due to the thin passive film that forms on the steel surface.³⁾

On the other hand, chloride ions can damage the passive film and induce localized corrosion. The mechanism of Cl⁻ intrusion into concrete invariably involves both capillary suction and diffusion; however, the transport depth associated with capillary suction is normally relatively shallow compared to the reinforcement cover, in which case diffusion alone is assumed. Once in the concrete, chlorides may exist as free ions or bound hydration products.^{4,5)} Reinforcing steel embedded in concrete begins to depassivate when a certain critical concentration of chloride ions, termed the chloride threshold, Cl_{th}^- , accumulates at the steel surface.⁶⁾ Values for Cl_{th}^- in the range 0.60~0.75 kg/m³ have historically been reported and referenced for concrete structures in North America.^{7,8)} However, this parameter, Cl_{th}^- , is now recognized as depending upon multiple factors, including 1) concrete mix design (water-to-cement ratio, cement content, and cement alkalinity)⁹⁾, 2) exposure conditions, and

* Corresponding author

Tel.: 82-51-410-4266 Fax.: 82-51-404-3985

E-mail address: corr@mail.hhu.ac.kr

3) reinforcing steel surface condition.¹⁰⁾ Accordingly, Glass and Buenfeld reported from a review of the literature to be in the range of 0.1~2.5 (total Cl⁻ on a cement w/o basis) or, alternatively, 0.66~9.71 kg/m³ (concrete weight basis assuming 400 kg/m³ cement content).¹¹⁾

While it is generally thought that Cl⁻_{th} increases with increasing alkalinity, no systematic investigations of this interrelationship have been performed. If alkali silica reaction (ASR) is not a factor and Cl⁻_{th} for high alkalinity cements exceeds that for normal ones, then use of high alkalinity cements should yield concrete structures with enhanced resistance to Cl⁻ induced corrosion but with no additional material cost or construction complexity. The objective of the present research was to perform a systematic study to evaluate the extent to which high alkalinity cement in concrete elevates Cl⁻_{th} and thereby provides enhanced corrosion resistance to embedded steel.

2. Experimental procedure

2.1 Specimen design and exposure

A total of 91 G109 type specimens¹²⁾ were fabricated where design variables included 1) cements with three alkalinities (equivalent alkalinities, EqA, 0.36, 0.52, and 0.96), 2) three water-to-cement ratios (0.37, 0.41, and 0.50), 3) presence versus absence of fly ash, and 4) presence versus absence of coarse aggregate.

Table 1 lists the composition of each cement. Subsequently, specimens based upon the EqA 0.36 cement are designated as “low” alkalinity or LA, the 0.52 cement as “normal” or NA, and the 0.97 as “high” or HA.

Table 2 provides the concrete mix design, and Table 3 lists the specimen categories. Seven specimens were fabricated for each mix design, four of which contained reinforcing steel according to the standard G109 configuration and there were no reinforcement. Diameter of the reinforcing steel was 12.7 mm, and the surface was wire-brushed just before placement.

Fig. 1 schematically illustrates the standard G109 specimen geometry. Concrete cover for the top and bottom bars was 25mm, and the bars were electrically connected through a 100 Ω resistor to facilitate measurement of macro-cell current. A plastic container was mounted on the top face of each specimen for ponding.

To control the direction of water and Cl⁻ flux, the four vertical sides of specimen (except bottom) were coated with epoxy. A one week wet-one week dry top surface ponding cycle began on June 3, 1998 using a 15 w/o sodium chloride solution.

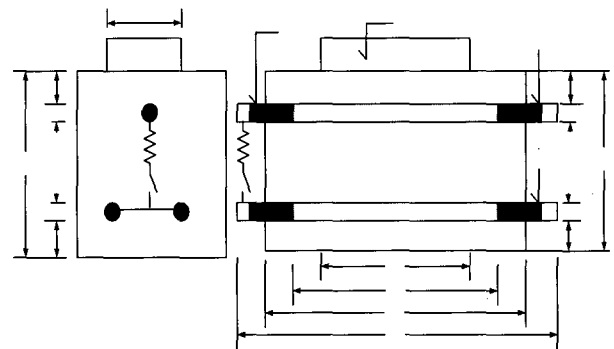


Fig. 1 Geometry of classical G109 specimen

Table 1 Compositions of cement type

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	EqA
LA	21.93	5.16	3.7	65.02	1.39	2.38	0.099	0.39	0.36
NA	21.88	5.64	3.87	64.42	0.98	2.87	0.164	0.54	0.52
HA	20.63	4.44	2.56	63.39	3.85	3.96	0.192	1.19	0.97

Table 2 Mix design of G109 specimen

Cement alkali	w/c	Cement(II) (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	Stone (kg/m ³)	Fly ash (kg/m ³)	WRDA-64 (kg/cwt)	WRDA-10 (kg/cwt)
LA	0.37	388.4	143.5	742.9	980.1	0	0.17	0.57
NA	0.41	388.4	159.0	702.0	980.1	0	0.17	0.43
HA	0.50	388.4	193.9	610.0	980.1	0	0.17	0
NAF	0.37	310.7	143.5	742.9	980.1	77.6	0.17	0.57
	0.41	310.7	159.0	702.0	980.1	77.6	0.17	0.43

Normal alkalinity cement (20% volume of cement replaced by fly ash)

Table 3 The list of the specimen configuration

Specimen no.	w/c	Rebar	Cement alkali	Ponding solution	Specimen no.	w/c	Rebar	Cement alkali	Ponding solution
01~04	0.37	Yes	High	15% NaCl	43~46	0.37	Yes	Low	15% NaCl
05~07		No			47~49		No		
08~11	0.41	Yes			50~53	Yes			
12~14		No			54~56	No			
15~18	0.50	Yes			57~60	Yes			
19~21		No			61~63	No			
22~25	0.37	Yes	Normal	15% NaCl	64~67	0.50	Yes	High Grout	15% NaCl
26~28		No			68~70		No		
29~32	0.41	Yes			71~74	Yes			
33~35		No			75~77	No			
36~39	0.50	Yes			78~81	Yes			
40~42		No			82~84	No			

2.2 Experimental measurements and definition of corrosion onset

At the end of the drying cycle, potential and macro-cell current were measured for each reinforced specimen to indicate whether the top steel was in a passive or active state. Active corrosion was defined as having commenced if, for two consecutive data acquisition periods, the macro-cell current was 10 μ A or greater and potential for the top bar was $-0.28 V_{SCE}$ (SCE: Saturated Calomel Electrode) or more negative.¹³⁾

Later, this definition was relaxed, and active corrosion was defined solely in terms of the potential criterion ($-0.28 V_{SCE}$).

2.3 Chloride concentration and pore water alkalinity determination

When specimens became active, they were autopsied; and concrete powder was collected by drilling about 1 mm into the upper trace of the top rebar at both corroded and uncorroded locations. At certain exposure intervals, vertically aligned concrete cores (5 cm diameter) were taken from the blank specimens. These were then sliced to give 5 mm thick sections to a depth of 70 mm, and the individual slices were ground to powder. Titration for $[Cl^-]$ determination was performed using the FDOT (Florida Department of Transportation, US) acid soluble method.¹⁴⁾ To determine the effective diffusion coefficient, D_e , the $[Cl^-]$ profiles acquired from the blank specimens were employed in a least squares curve-fitting algorithm of the one-dimensional solution to Fick's second law,

$$\frac{C(x, T) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D_{eff} \cdot T}}\right) \quad (1)$$

where, $C(x, T)$ is chloride concentration at depth x after time T , C_o is initial or background $[Cl^-]$ in the concrete, and C_s is the $[Cl^-]$ at the exposed surface. Assumptions involved in this procedure were that, first, C_s and D_e were constant with time and, second, the diffusion was "Fickian"; that is, there were no Cl^- sources or sinks in the concrete.

For pH measurement, samples were collected from mid-way between the top and bottom of specimens to minimize the risk of carbonation and to ensure that little or no Cl^- would be present. An ex-situ leaching procedure that was developed previously was employed.¹⁵⁾ Basically, this involved mixing about 50 g of concrete powder with 50 ml of de-ionized water for 3 days. During the leaching, the mixtures were stirred from time to time. At the end of leaching period the sample was filtered to remove residual solid particles. The solution was then titrated for both OH^- and Ca^{2+} , and pH was calculated from the expressions,

$$pH = 14 + \log(\gamma[OH^-]_{pore}), \quad (2)$$

where, γ is the activity coefficient of OH^- , which is approximately 0.7 when $[OH^-]_{pore} > 0.1 \text{ mol/L}$.¹⁶⁾

3. Results and discussion

3.1 Onset of corrosion

As of May 2003, 28 of the 48 reinforced G109 specimens had exhibited active corrosion. Table 4 provides a listing of all reinforced specimens and of time-to-corrosion (T_i) values in the cases of corrosion activity.

In instances where T_i was relatively brief, the potential shift from the range of passivity ($\geq -0.10 V_{SCE}$) to that of active corrosion ($\leq -0.28 V_{SCE}$) was relatively abrupt. Concurrently, macro-cell current increased from negligible to

greater than $10 \mu\text{A}$. In the case of specimens for that corrosion initiated after a relatively long exposure time, this change was more gradual with specimens often reverting to the passive state. Fig. 2 presents current versus time data for specimens of the LA0.50 mix design, which exemplifies the former type of behavior. Fig. 3 presents comparable data for the HA 0.41 mix design, which typifies the latter. For specimens in the second category, corrosion was considered to have initiated at the time when potential first became more negative than $-0.28 \text{ V}_{\text{SCE}}$, irrespective of any subsequent,

more positive potential drift. Macro-cell current was often less than $10 \mu\text{A}$ at this time (see Fig. 3).

3.2 Pore water alkalinity

Fig. 4 shows results of the pore water pH determinations as a function of cement alkali content (w/o cement) and with

Table 4 The list of time to corrosion (Ti) of reinforcing steel concrete

Specimen no.	Mix design	Ti (days)
1	HA0.37	>1800
2	HA0.37	>1800
3	HA0.37	>1800
4	HA0.37	>1800
8	HA0.41	>1800
9	HA0.41	1329
10	HA0.41	1192
11	HA0.41	1401
15	HA0.50	136
16	HA0.50	306
17	HA0.50	297
18	HA0.50	225
22	NA0.37	>1800
23	NA0.37	>1800
24	NA0.37	1096
29	NA0.41	136
30	NA0.41	206
31	NA0.41	339
32	NA0.41	1120
36	NA0.50	93
37	NA0.50	93
38	NA0.50	136
39	NA0.50	178
43	LA0.37	>1800
44	LA0.37	>1800
45	LA0.37	190
46	LA0.37	>1800
50	LA0.41	297
51	LA0.41	>1800
52	LA0.41	567
53	LA0.41	>1800
57	LA0.50	107
58	LA0.50	234
59	LA0.50	136
60	LA0.50	136
64	HAG0.50	149
65	HAG0.50	178
66	HAG0.50	107
67	NAF0.37	>1800
71	NAF0.37	>1800
72	NAF0.37	>1800
73	NAF0.37	>1800
74	NAF0.37	>1800
78	NAF0.41	>1800
79	NAF0.41	>1800
80	NAF0.41	>1800
81	NAF0.41	>1800

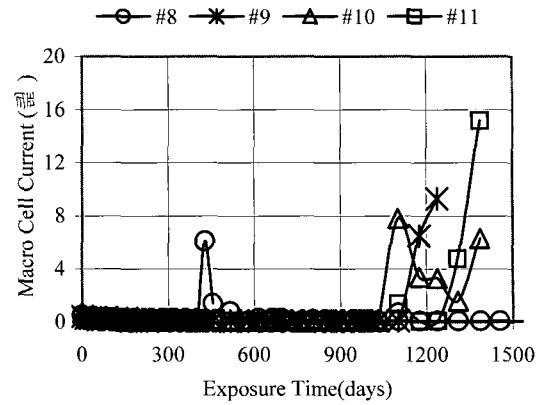


Fig. 2 The current change of LA0.50 type specimens

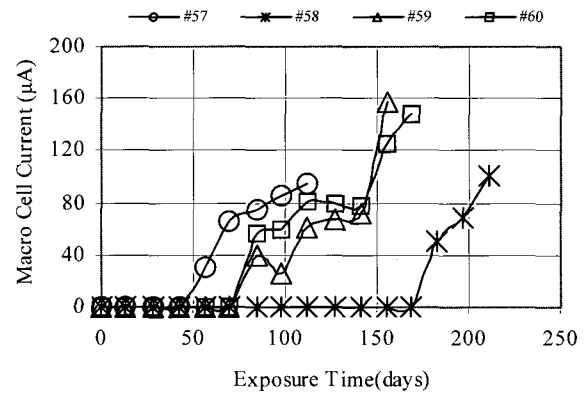


Fig. 3 The current change of HA0.41 type specimens

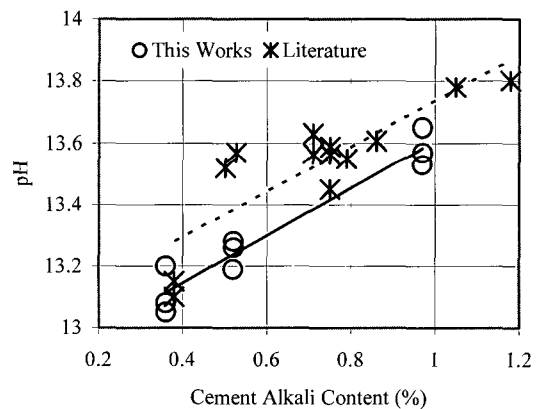


Fig. 4 The pore water pH as a function of cement alkali content and data from the literature¹⁷⁻²⁶⁾

data from the literature¹⁷⁻²⁶ that are based upon pre-water expression experiments included for comparison. This shows that pH increased in direct proportion to cement alkali content and that pH data for the present specimens ranged from 13.05 to 13.20 for the LA mix, 13.19 to 13.36 for the NA, and 13.53 to 13.65 for the HA with the present data occupying the lower bound of the literature results.

3.3 Diffusion coefficients

Fig. 5 presents a plot of D_e versus EqA with the data partitioned according to w/c. Cores for the D_e determinations were taken at about 1,200 and 1,600 days exposure except for the w/c = 0.50 case where the core was taken at 133 days. These results indicate less Cl^- penetration rate for highest alkalinity mix compared to the lower equivalent alkalinity (EqA) ones. For example, D_e for EqA = 0.97 (HA) was lower than for EqA = 0.52 (NA) and 0.36 (LA) by approximately 40 percent. The reason why the chloride D_e was lower in HA type specimens compared to the NA and LA

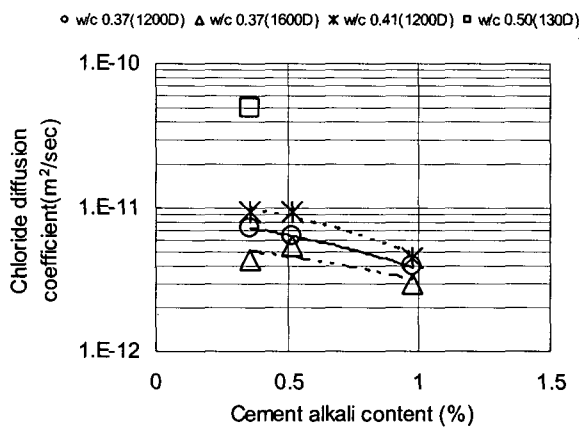


Fig. 5 The relationship between effective chloride diffusion coefficient (D_e) and equivalent cement alkalinity (EqA)

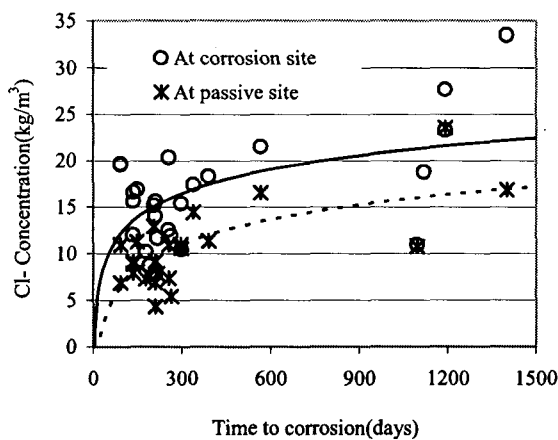


Fig. 6 Chloride thresholds (Cl^-_{th}) with respect to time to corrosion (T_i)

may be related to Cl^- activity. According to Francy et al.²⁷⁾ and Achari et al.²⁸⁾ chloride diffusivity decreases as pore water concentration increase. This can be explained by the fact that an increase of solution ion concentration increase ion activity, hence reducing the diffusion rate.

3.4 Chloride threshold concentration

Table 5 lists chloride concentration $[Cl^-]$ values that were measured for powdered concrete samples acquired along the upper region of the top rebar trace, both at the active corrosion site and elsewhere where the steel remained passive. Also, listed are T_i and the exposure time at which active specimens were autopsied. From these times and the D_e values, the $[Cl^-]$ at the time individual specimens became active was back-calculated; and this value was taken as Cl^-_{th} . Fig. 6 shows a plot of Cl^-_{th} versus T_i and indicates that in most cases $[Cl^-]$ for the active corrosion sites at the time of initiation exceeded that where the steel remained passive. However, $[Cl^-]$ at the active and passive sites was approximately the same in some cases (Specimen No. 24 and 50 underlined) where autopsy was performed shortly after

Table 5 Chloride concentration at corrosion site and passive state

No.	$[Cl^-]$ Active	$[Cl^-]$ Passive	T_i	Autopsied time
10	23.27	23.53	1192	1459
11	33.50	16.82	1401	1455
15	11.98	8.92	136	211
16	15.39	10.59	306	324
17	18.28	11.32	297	433
18	12.54	10.92	225	319
24	<u>10.93</u>	<u>10.76</u>	<u>1096</u>	<u>1124</u>
25	27.64	-	1192	1229
29	15.63	7.92	136	211
30	15.81	12.86	206	256
31	17.39	14.41	339	381
32	18.76	-	1120	1186
37	19.56	6.90	93	213
38	16.62	9.13	136	256
39	10.22	7.29	178	211
45	16.90	11.22	190	211
50	<u>10.44</u>	<u>10.95</u>	<u>297</u>	<u>324</u>
52	21.46	16.49	567	576
58	11.87	5.42	234	264
59	15.61	4.31	136	211
60	20.33	7.37	136	190
64	8.70	7.59	149	190
65	7.84	6.87	178	211
66	11.64	7.84	107	217
67	13.99	9.18	163	211

* Concentration unit kg/m^3 and time unit is days

potential first became negative to $-0.28 V_{SCE}$. This suggests that the elevated $[Cl^-]$ at the corrosion site resulted from electro migration subsequent to corrosion initiation. If this was the case, then it is the remote site $[Cl^-]$ that should be taken as Cl_{th} .

The general trend in Table 5 and Fig. 6 is one where Cl_{th} increased with time, albeit at a progressively decreasing rate, irrespective of mix design. Thus, while specimens of low cement alkalinity and high w/c exhibited the shortest T_i and vice versa, all data conform to a common trend with time. This is consistent with, first, chlorides having continued to progressively accumulate with increasing time and, second, T_i being a statistically distributed parameter. Fig. 7 shows a plot of Cl_{th} versus pore water alkalinity ($M[OH^-]$) and indicate that an increase in the latter parameter elevated the former according approximately to a linear trend irrespective of T_i . The improved T_i for HA type specimens compared to type LA and NA can be explained by this elevated Cl_{th} . However, LA type specimens revealed longer T_i than that of NA ones, the reason might be higher chloride binding capacity of low alkalinity cement than Normal one.²⁹⁾

As noted above, values for Cl_{th} in the range $0.60\sim 0.75 \text{ kg/m}^3$ have historically been reported and are widely referenced in North America concrete deterioration studies.^{7, 8)} Also, the upper limit of Cl_{th} values reported by Glass and Buenfeld (9.71 kg/m^3 w/o concrete)¹¹⁾ approximates the mid-value determined from the present exposures. Possible explanations for the present, relatively high Cl_{th} values include (1) surface condition of the reinforcement (wire brushed as opposed to as-received), (2) absence of relative humidity (RH) and temperature variations during the laboratory exposures, and (3) specimens were relatively small such that the nature of the steel-concrete interface may not reflect statistically the variability that can arise in large structures. With regard to surface condition of the reinforcement, Li and Sagüés¹⁰⁾ found, based upon exposure of carbon steel in simulated pore water solutions (pH: 12.6~13.6), that Cl_{th} for as-received and pre-rusted reinforcing steel specimens in simulated pore solutions was approximately half that of sandblasted ones. If performance of specimens with a wire brushed surface finish, as was the case for the present bars, is comparable to that for sandblasted ones and if results from aqueous exposures can be quantitatively compared to those for steel in concrete, then this surface preparation distinction between the present bars and ones used in actual structures, which are likely to be prerusted could have contributed about a factor of two of the difference between the present and previously reported Cl_{th} values.

In the case of item (2), it can be reasoned that temperature/RH variations, as occur with outdoor conditions, promote fluxes of moisture and oxygen in concrete that do not take place under controlled laboratory situations and that

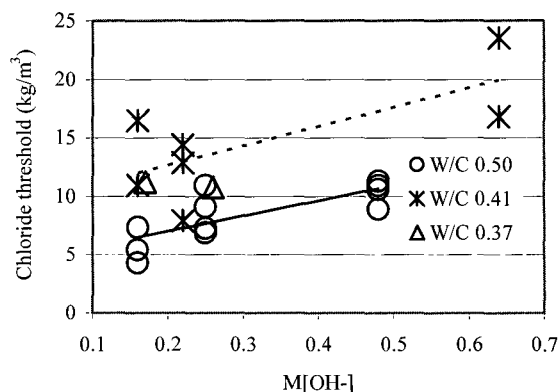


Fig. 7 Chloride thresholds (Cl_{th}) with respect to $M[OH^-]$

these, in turn, facilitate the onset of corrosion.

However, no data are available from the present experiments that can provide a determination of the role of this factor. Concerning item (3), previous research has reported that corrosion of reinforcing steel preferentially initiates at concrete voids that impinge upon the steel.³⁰⁾ More recently, Mohammed et al.³¹⁾ reported Cl_{th} values in excess of two percent (w/o cement) when the concrete-steel interface was compact. Visual observation of the initial specimens that became active in this study revealed one or more air voids at the site of active corrosion.

4. Conclusions

The following conclusions were reached based upon exposure of a series of G109 specimens to cyclic wet-dry ponding with a 15 w/o NaCl solution.

- 1) Time-to-corrosion was a distributed parameter; and because of this, corrosion initiation for "identical" specimens of each mix design varied, often over a relatively wide range. Time for the onset of active corrosion, T_i , was least for ones that were of normal alkalinity (EqA 0.52), intermediate for a low alkalinity (EqA 0.36), and highest for high alkalinity (EqA 0.97) cement.
- 2) Pore water pH was in the range 13.05 ~ 13.20 for the LA mix concrete, 13.19 ~ 13.36 for the NA, and 13.53 ~ 13.65 for the HA. This amounted to OH^- concentration for the HA cement concrete being about a factor of two greater than for the NA.
- 3) The effective Cl^- diffusion coefficient, D_e , increased with increasing water-cement ratio and was about 40 percent lower for concrete prepared with the HA cement compared to the NA and LA ones. This may have resulted from reduced Cl^- activity in pore water of the HA cement mix specimens.
- 4) The chloride threshold concentration increased with increasing T_i . Consequently, the HA specimen exhibited the highest Cl_{th} and the NA the least. Local chloride

concentrations in the concrete measured from powder drillings taken along the rebar trace varied from 7.84 to 27.64 kg/m³ (concrete w/o basis) at the site of active corrosion and from 4.31 to 23.52 kg/m³ at locations where the steel was passive. The latter range is considered to represent Cl_{th}, and it is in the upper range of Cl_{th} values that have been reported in the literature.

- 5) In situations where observations were made, corrosion was often found to have initiated at an air void in the concrete that intersected the reinforcement. A concentration cell whereby the contiguous concrete coated and bare steel served as cathode and anode, respectively, is considered to have been resulted. The size and density distribution of these voids may have contributed to or been responsible for the finding that T_i was a distributed parameter.

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