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Characterizing the Effect of Concrete Mix-design on Sorptivity of Chlorides

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ABSTRACT

This paper characterizes the effect of concrete mix-design on sorptivity of chlorides, in reinforced concrete exposed to cyclic wetting and presents the relationship between concrete mix-design and the apparent surface-content of chloride. Specimens of concrete of different relative water to cement ratio are prepared, cured and immersed after 28-days of curing. Absorption or sorption, in combination with diffusion, is examined as a transport mechanism for dissolved ions of both chlorides and carbon dioxide into concrete exposed to cyclic rainfall. From research, it is evident that diffusion alone can no longer explain the increasing depths of penetration of ions of chlorides into concrete, under cyclic wetting and drying weather. This is because concrete mix-design affects very significantly, the durability of reinforced concrete exposed to cyclic weather. Durability characteristic of exposed concrete structure is threatened by an ever increasing depth of chlorides ingress and corrosion of rebar as a direct consequence of the rising contents of chloride ions. The results show that there is a linear relationship between the rate of change in apparent surface-content of chloride and unity less the water to cement ratio of concrete.

Keywords: *Chlorides in concrete, concrete mix-design on surface-content of chlorides, Chlorides sorption of concrete.*

1.0 INTRODUCTION

It is believed that chlorides enter concrete initially by capillary suction and produce a reservoir of chloride ions a relatively short distance from the surface, from which diffusion occurs [Hong & Hooton, 1999]. The influence of concrete quality (or concrete mix-design) is an important factor in resisting chloride sorption [Polder and Peelen, 2002]. Even so, the quality of concrete can have a very important effect on the pore structure (Pocock & Bamforth, 1991). And the penetration of rain-soluble ions of Carbon dioxide and chloride into concrete appear to depend on the water to cement quality of concrete (Frederiksen, 1996) and more so, on the relative water to cement ratio of concrete.

Here, the initial transport mode appears to be suction but, once the surface is dry, chloride solution is rapidly absorbed by dry concrete via diffusion [Hong & Hooton, 1999]. When concrete dries out to a greater depth, subsequent rainfall carry the chlorides deeper into the concrete [Hong & Hooton, 1999] and this reservoir is continuously recharged by cyclic sorption of rain soluble chlorides.

This capillary suction followed by diffusion, causes a mixed transport mode in concrete. However, both mechanisms depend on pore structure of concrete. At a simplistic level, it is assumed that any rise in apparent surface-content of chloride depends mostly on both on the physical nature of concrete, whereby more porous concrete allows the sorptivity of greater quantity of free ions of chloride into the concrete [Polder and Peelen, 2002]. This is because the influence of concrete mix design on the value of apparent surface-content of chloride ions is very complex (Pocock & Bamforth, 1991).

Therefore, this research is aimed at characterizing the effect of concrete mix-design on sorptivity of chlorides, in reinforced concrete exposed to cyclic wetting and drying.

2.0 DETERIORATION ANALYSIS

2.1 TIME-LAWS OF CHLORIDE-INGRESS:

The rate of deterioration of concrete exposed to cyclic wetting/drying as a result of sorption coupled by diffusion, can be expressed by a differential equation based on Fike's second law:

$$\frac{\partial C}{\partial t} = \mathrm{D}\frac{\partial^2 C}{\partial x^2} = \mathrm{R_o} \qquad (1.1)$$

where, R_o – is the rate of deterioration or effective coefficient of deterioration of concrete exposed to wetting and drying, as a result chloride attack. *D* - is the effective diffusivity of chlorides in concrete depending on binder composition, [in m^2/s or in $mm^2/year$].

Then, Crank's error-function solution to differential equation (1.1), can be expressed following the operational model by Alisa et al, 1998, and it
approximates the time law of chloride-ingress, as a result of sorption coupled with diffusion, thus: $\frac{C}{C's} = [1 - \text{erf}\,[\frac{Xcc}{2\sqrt{(Dt)}}]]$ (1.2)
Where erf – is the Gaussian error function.

Transiting from Crank's error-function solution in equation (1.2), to Bazant's parabola-function solution, the time laws of chloride-ingress in equation (1.1) can approximately be expressed as:

$$\frac{C}{C's} = [1 - \frac{Xcc}{2\sqrt{(3Dt)}}]^2 \qquad (1.3)$$

Where, **C** - denotes the total content of chloride ions within concrete at the depth X_{cc}, when background chloride content is nil, in % wt of cement. D - is the effective diffusivity of chlorides in concrete depending on binder composition, in $mm^2/year$. C'_s – is the apparent surface content of chlorides in concrete exposed to wetting and drying as a result of sorption coupled with diffusion, in % wt. of cement. The apparent surface content of chloride ions can be determined by adjusting representative chloride profiles along Crank's error function solution and extrapolating the resulting chloride profile-curve to concrete surface. X_{cc} – Denotes the cover thickness loss *ctl* of the concrete exposed to wetting and drying, due to chloride attack, in mm. t – Denotes exposure time, in years.

2.2 ACCEPTABLE THRESHOLD FOR CORROSION ONSET:

The critical value of chloride adopted for corrosion-initiation is the recommended value by Glass and Buenfeld 1997; Ballim *et al.,* 2009. It should be noted that the acceptability coefficient (or the size factor) is not included in the recommended chloride threshold, however, it should be understood that:

$$C = C_{crit} \qquad (1.4)$$

C_{crit} – is the acceptable threshold or critical value of chloride for corrosion initiation.

Thus, by replacing **C** in equation (1.3) with $\mathbf{C_{crit}}$, in equation (1.4) and re-arranging equation (1.3):

$$\frac{\mathrm{Ccrit}}{\mathrm{C's}} = \left[1 - \frac{Xcc}{2\sqrt{(3Dt)}}\right]^2 \qquad (1.5)$$

2.3 SURFACE CONTENT OF CHLORIDES:

2.3.1 Effect of Carbonation on Chlorides Sorptivity:

For unsaturated concrete exposed to cyclic wetting and drying, the result of experimental observations shows that carbonation rate in medium to high quality concrete is much less than the rate of chloride penetration, in all exposure condition. Except in poor quality concrete exposed to marine atmosphere, where the rate of carbonation can be exceptionally very high especially in dry climates (Costa & Appleton, 2001). Variation in apparent surface-content of chlorides on account of carbonation can be avoided altogether by use of high quality concrete and relevant rebar cover. Nevertheless, protection of concrete from the combined effect of carbonation with chlorides shows that with high quality concrete, carbonation is negligibly of little significance (Costa & Appleton, 2001).

EFFECT OF CONCRETE QUALITY (MIX-DESIGN) ON SORPTIVITY:

(A) Basic Hypothesis and Model Algorithm.

In concrete exposed to cyclic wetting and drying, the influence of concrete mix design otherwise called the quality of concrete on sorptivity of chlorides can strongly affect concrete (Pocock & Bamforth, 1991). However, the apparent surface-content of chlorides $\mathbf{C'_s}$ in concrete exposed to cyclic wetting and drying, as in figure 1.1, becomes:

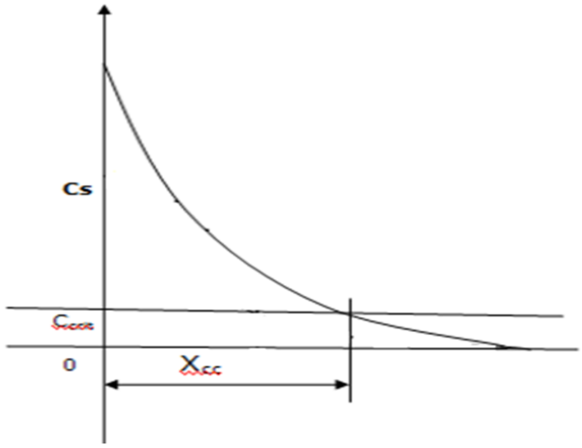

Figure 1.1 –Schematic of chloride profiles in concrete.

Characterizing the effect of concrete quality (or concrete mix-design) on the ingress of chlorides via capillary sorption, let the water to cement ratio of concrete be adopted, because there is a linear relationship between concrete mix-design (or concrete quality) and its water to cement ratio. Incidentally, the relationship between the apparent surface-content of chlorides and the water to cement ratio of concrete is also linear (Frederiksen, 1996). And capillary sorption decreases with decreasing water to cement ratio of concrete [Parrott, 1992; Dhir et al, 2004; Kolias & Geargio, 2005]. The concrete mix-design on sorptivity of chlorides results in chloride penetration decreases as the water to cement ratio of concrete decreases.

Therefore, increase in apparent surface content of chloride, as a result of the effect of concrete mix-design on sorptivity will be proportional to the relative increase in penetrated ions of chlorides, as can be illustrated graphically in fig. 1.2.

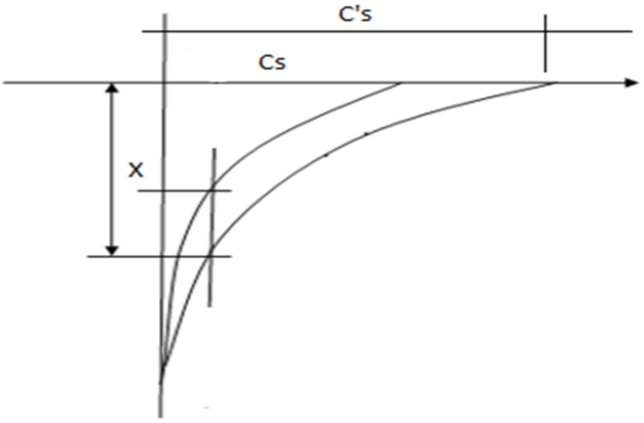

Fig 1.2 –Schematic of the rise in apparent surface-content of chlorides.

As a consequence of the foregoing, let: $\frac{C's - \mathrm{Cs}}{\mathrm{C's}} = \frac{\Delta l}{\Delta}$ (1.6)

Where, $(C's - \mathrm{Cs})$ - represent the difference between the apparent surface-content of chlorides as a result of sorption coupled with diffusion and surface content of free chlorides, in concrete exposed to diffusion. $\boldsymbol{\Delta l}$ - is assumed to represent the quantity of movable free chlorides as a result of the effect of concrete mix-design on chlorides sorptivity.

Δ – is the sum total of all movable free chlorides, in concrete exposed to cyclic wetting and drying, as a result of sorption coupled with diffusion.

$\mathbf{C's}$ – is the apparent surface-content of chlorides in concrete exposed to cyclic wetting and drying, as a result of sorption coupled with diffusion. Cs – is the surface content of free chlorides, in concrete exposed to diffusion.
By re-arranging equation (1.6):

$$\frac{\mathrm{Cs}}{\mathrm{C's}} = \left(1 - \frac{\Delta l}{\Delta}\right) \qquad (1.7)$$

$$\mathrm{C's} = \mathrm{Cs}\left(1 - \frac{\Delta l}{\Delta}\right) \qquad (1.8)$$

Where $\left(1 - \frac{\Delta l}{\Delta}\right)$ – is the modifier to **Cs.**

(B) Time Dependency of $\mathbf{C's}$:

Since the apparent surface-content of chlorides **C's** increases continuously with exposure time in saturated and unsaturated concrete (Tang & Gulikers 2007; Tang & Nilsson 2000; Thomas & Bentz 2000; Kim & Kim, 2010) alike, then $\mathbf{C's}$ is time-dependent, especially in concrete exposed to cyclic wetting and drying. However, Kassir & Ghosn, (2002), showed that time-dependency of apparent surface-content of chlorides can be expressed by an exponential variation of with time such that:

$$f_{(t)} = (1 - e^{-gt}) \qquad (1.9)$$

where the exponent (- gt) is a product of the rate of change per year and time of exposure in years.

By implication however, the time function $f_{(t)}$ could be approximated as did in Kim & Kim (2010) as: $f_{(t)} = \frac{(t)}{(tref=1)} = t.$ (1.10)

where t – is the duration of exposure in years per year.

The implication of combining equations (1.8) with (1.10), gives the time dependency of $C'_{s(t)}$ expressed as thus:

$$C'_{s(t)} = Cs.\,(1 - \frac{\Delta l}{\Delta})\, t \qquad (1.11)$$

By letting the multiplier of **Cs** above:

$$(1 - \frac{\Delta l}{\Delta})\, t = t^{v} \qquad (1.12)$$

Where (**v**) – is an exponential modifier denoting the rate of change in apparent surface chloride per year, in t-years, as a result of the influence of concrete mix-design on sorptivity of chlorides, when sorption is coupled with diffusion.

Recalling equation (1.11) above:

$$C'_{s(t)} = Cs\,.\,t^{v} \qquad (1.13)$$

Assuming that the exponential modifier (**v**) is correlated to the expression $(1 - \frac{w}{c})$ with a coefficient of correlation less than unity, and reflecting the influence of concrete mix-design on sorptivity of chlorides, then, the relationship between both values can be expressed as:

$$v = (1 - \frac{w}{c}) \qquad (1.14)$$

where $\frac{w}{c}$ - is the water to cement ratio of concrete which characterizes the effect of concrete mix-design on chlorides sorptivity.

3.0 VERIFICATION EXPERIMENT

Experimental simulations for generating comparative data involving the use of parameters computed from material history and advanced model.
This comparative data is particularly useful because it supplies the basis for logical acceptance or rejection of research hypothesis.

3.1 Exposure Condition in Experimental Environment:

For purposes of this study, the weather condition is assumed to be approximately 6-months of wetting and 6-months of drying. The monthly averages of temperature and other parameters such as monthly content of dissolved chlorides in raindrops and monthly averages of relative humidity, within the exposure environment are found in table 1.1.

Table 1.1: Characteristics of the experimental environment

Conditions of exposure environment.	Wetting months = 9 Feb – Oct	Drying months = 3 Nov – Jan
Average monthly temp.	28^oC	32^oC
Average monthly Content of rain-borne chlorides, mg/l	30.6	-
Monthly Average of Relative Humidity	85%,	65%,

3.2 MATERIALS:

Four (4) batches of in-situ concrete of water to cement ratio 0.3 for mix-1; 0.4 for mix-2; 0.5 for mix-3 and 0.6 for mix-4, are made from Portland cement (CEM 11/A-L 42.5 R), river sharp sand and granite aggregates with sizes ≤ 19mm. A superplasticizer is added to mix-1 to enhance workability while reducing water consumption.

Table 1.2: Composition of concrete mixes for experimental verifications

	Mix 1	Mix 2	Mix 3	Mix 4
w/b ratio	0.3*	0.4	0.5	0.6
Cement, kg/m3	425	350	300	300
Sharp Sand, kg/m3	677	726	822	822
Granite, kg/m3	1231	1231	1231	1231
Water, kg	128	140	150	180
plasticizer	1.0	-	-	-

(*with plasticizer in amount 0.2% wt of cement)

3.3 EXPERIMENTAL PROCEDURE:

The experimental procedure adopted for this verification is similar to those adopted by Lee & Yoon, (2003). The procedure involves exposing concrete specimens to 12 consecutive cycles of 1-week wetting in PVC containing 0.5M of brine (i.e. water containing 5% NaCl2, filling over each specimen to at least 13mm) followed by 1-week drying in air containing 0.3% by volume of CO2 at 65% of relative humidity @ room-temperature, to simulate combined deterioration involving carbonation with chloride attack (Lee & Yoon, 2003). Prior to performing a combined deterioration procedure, manually determined data based on this model are obtained, to include the water to cement characteristics of concrete mixes, characteristic chloride diffusivities of concrete mixes constants as well as the calculated values of the apparent surface-content of chlorides for 1, 3 and 12-year. And these parameters are summarized in table 1.3.

4.0 RESULTS AND DISCUSSION

The purpose is to compare:

- The changing rate of **(v)** in table 1.4 and changing $(1 - \frac{w}{c})$ in table 1.3.

- The apparent surface-content of chlorides after 1, 3 and 12-years, as calculated using $\mathrm{Cs}\,.\,\mathrm{t}^{\left(1-\frac{w}{c}\right)}$ from model, in table 1.3 and experimentally determined Cs. $\mathrm{t}^{(v)}$, in table 1.4.

Table 1.3: Near-term Summary of material parameters from material history

		Mix 1	Mix 2	Mix 3	Mix 4
w/c ratio		0.3	0.4	0.5	0.6
$(1 - \frac{w}{c})$		0.7	0.6	0.5	0.4
D_c, mm^2/year		2.84	2.84	7.88	15.77
Cs @ 2-2.5mm ctrs. Experimentally determined from control specimen prior to carbonation, % wt of binder.		0.08	0.10	0.12	0.14
@ t = 1-year	$C'_{s(1)} = \mathrm{Cs}\,.\,\mathrm{t}^{\left(1-\frac{w}{c}\right)}$ % wt of binder	0.08	0.10	0.12	0.14
@ t = 3-years	$C'_{s(3)} = \mathrm{Cs}\,.\,\mathrm{t}^{\left(1-\frac{w}{c}\right)}$ % wt of binder	0.17	0.19	0.21	0.22
@ t = 12-years	$C'_{s(12)} = \mathrm{Cs}\,.\,\mathrm{t}^{\left(1-\frac{w}{c}\right)}$ % wt of binder	0.46	0.44	0.42	0.38

Table 1.4: Near-term Summary of experimentally simulated parameters

		Mix 1	Mix 2	Mix 3	Mix 4
w/c		0.30	0.40	0.50	0.60
V		0.68	0.61	0.54	0.46
$D_{ref} = k_t.\ D_{RCM}$, mm^2/year @28 days		2.80	2.81	7.87	15.64
Cs @ 2-2.5mm ctrs. Experimentally determined from control specimen prior to carbonation, % wt of binder.		0.08	0.10	0.12	0.14
@ t = 1-year	$C'_{s(1)} =$ Cs. $\mathrm{t}^{(v)}$, % wt of binder	0.08	0.10	0.12	0.14
@ t = 3-year	$C'_{s(3)} =$ Cs. $\mathrm{t}^{(v)}$, % wt of binder	0.17	0.20	0.22	0.24
@ t =12-year	$C'_{s(12)} =$ Cs. $\mathrm{t}^{(\mathrm{V})}$, % wt of binder	0.43	0.46	0.46	0.48

Table 1.5: Long-term comparison with laboratory simulations of deteriorations

		Mix 1	Mix 2	Mix 3	Mix 4
w/c		0.30	0.40	0.50	0.60
$(1 - \frac{w}{c})$		0.7	0.6	0.5	0.4
V		0.68	0.61	0.54	0.46
D_c, mm^2/year		2.84	2.84	7.88	15.77
$D_{ref} = k_t.\ D_{RCM}$, mm^2/year @28 days		2.80	2.81	7.87	15.64
Cs @ 2-2.5mm ctrs. Experimentally determined from control specimen prior to carbonation, % wt of binder.		0.08	0.10	0.12	0.14
$f_{(s)}\ f_{(T)}\ f_{(a)} = 0.29$ @ t = 50-year	$C’s_{(50)} = Cs\ .\ t^{\left(1-\frac{w}{c}\right)}$ % wt of binder	1.2	1.0	0.8	0.7
	$C’s_{(50)} = Cs.\ t^{(v)}$, % wt of binder	1.1	1.1	1.0	0.8
$f_{(s)}\ f_{(T)}\ f_{(a)} = 0.29$ @ t = 100-year	$C’s_{(100)} = Cs\ .\ t^{\left(1-\frac{w}{c}\right)}$% wt of binder	2.0	1.6	1.2	0.9
	$C’s_{(100)} = Cs.\ t^{(v)}$, % wt of binder	1.8	1.7	1.4	1.2

For these particular compositions of concrete, both near and longer-term simulation using advanced model and experimental verifications are compared. For exposure durations greater than 12-years, especially for concrete having w/c ratio 0.3; 0.4; 0.5 and 0.6, the rate of change in apparent surface-content of chloride v is constantly equal to unity less the water to cement ratio of concrete $(1 - \frac{w}{c})$. This implies that the apparent surface chloride increases as the water to cement ratio of concrete decreases and the ingress of chlorides into concrete exposed to cyclic wetting and drying depends on the mix-design of the concrete. These comparisons show good agreement between advanced model and experimental verification. The slight variations are tolerable and cannot be of any consequence in the long run.

5.0 CONCLUSION

However, indicated good agreement between simulated and calculated results show that there is a correlation between the rate of change in apparent surface-content of chloride **v** and unity less the water to cement ratio of concrete ($1 - \frac{w}{c}$). And that corrosion-induced deterioration of concrete exposed to cyclic wetting and drying which is a function of chlorides sorptivity of concrete can simply and reasonably be said to depend on the quality of concrete or concrete mix-design. It could be seen also that the apparent surface chloride increases as the water to cement ratio of concrete decreases. Therefore, the ingress of chlorides into concrete exposed to cyclic wetting and drying depends on the mix-design of the concrete. These are plausible explanation for the comparatively faster corrosion-deterioration experienced by poor quality structural concrete, exposed to rainfall in the warm and humid zone.

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