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Actual and Effective Diffusion Coefficients of Concrete Under Marine Exposure Conditions

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ACTUAL AND EFFECTIVE DIFFUSION COEFFICIENTS OF CONCRETE UNDER MARINE EXPOSURE CONDITIONS

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1. Background
Chloride ions, arising from marine exposure or the use of de-icing salts, are a recognized threat to the durability of reinforced concrete. If the chloride penetrates the concrete cover in sufficient concentration the potential for corrosion of mild steel reinforcing is greatly enhanced. The resulting loss of reinforcing section and spalling of cover concrete is, at best, cosmetically unattractive and, at worst, a threat to the structural integrity of the design.

Penetration of the cover concrete can occur by chloride ions being transported through the porous concrete matrix by a variety of different physio-chemical processes. An often cited example considers a seawall: Below the low tide mark, where the concrete is permanently submerged, chloride ions diffuse through the saturated pore structure of the concrete in response to concentration gradients. Above the high tide mark, where waves irregularly splash relatively dry concrete, absorption due to capillary suction predominates. Behind the seawall, brackish ground water may permeate the concrete driven by hydrostatic pressure.

1.1 Fick’s Law
Despite this range of possible transport mechanisms, chloride ingress of concrete is almost inevitably analysed using the language and mathematics of diffusion. This is primarily a matter of pragmatism - a plot of chloride concentration vs. penetration depth can often be closely described by Crank’s solution to Fick’s 2nd Law of Diffusion.

Crank’s solution states that the chloride concentration in the concrete \( C_x \), at any depth \( x \) below an exposed surface is a function of the boundary surface chloride concentration \( C_s \), an intrinsic chloride diffusion coefficient for the concrete \( D \), and the period of exposure \( t \),

\[
C_x = C_s \times erfc\left(\frac{x}{\sqrt{4Dt}}\right)
\]  

\( C_s \) quantifies the chloride load or severity of the exposure conditions and \( D \) the resistance of the concrete to penetration, while \( erfc \) is the mathematical Gaussian error function complement. The equation assumes the surface to be plane and the area and depth to be effectively infinite.

In a pure application of diffusion theory to a porous material such as concrete, Crank’s solution would describe the concentration of the chloride ions in the pore solution directly. However, because extraction and analysis of the pore fluid is difficult, chloride ingress profiles are usually obtained by milling discrete increments of concrete at specified depths from the surface. The resulting powders are then analysed for their total chloride concentration. This value includes both the free ions in the pore fluid and those that are physically absorbed onto, or have chemically reacted with, the cement gel. Recent research by Glass suggests that total chloride is in fact the most appropriate parameter for determining risk of reinforcement corrosion. However the action of...
chloride binding has some initially unexpected consequences. For example, the boundary $C_s$ value for concrete completely submerged in seawater is not equal to the chloride concentration of the brine, but also depends upon the concrete’s cement type, total porosity and even surface finish and curing.

1.2 Practical application of Fick’s Law

Crank’s solution is routinely applied in two ways which, although superficially similar, are quite distinct and need to be carefully distinguished. One application is in the determination of ‘actual diffusion coefficients’ (Here referred to as $D_{act}$ – note the terminology is not consistent through the literature). This is an attempt to measure the intrinsic diffusivity of concrete by a bulk immersion test, such as NT Build 443 in which a completely saturated specimen is immersed in seawater for 35 days. A diffusion coefficient is calculated from the developed chloride profile by applying non-linear regression analysis, which yields best-fit values for $D$ and $C_s$. This procedure is normally carried out on early-age (28 or 56 day old) test specimens for characterisation purposes, but can also usefully be performed on virgin core samples ( uncontaminated with chloride) from existing structures to determine the current diffusivity of the interior concrete.

For existing concrete structures where a chloride ingress profile has already developed through natural exposure to the environment it is possible to use equation (1) and the same curve fitting procedure to determine ‘effective diffusion coefficients’ ($D_{eff}$). This provides a method of characterising the historical performance of a particular concrete or structure. It may also be of value for indicating future performance, although recent studies show that the significant variations in chloride ingress that can be observed in a single structure makes accurate quantification of remaining service life difficult. $D_{eff}$ is distinct from $D_{act}$ both because it reflects the influence of all the possible transport mechanisms that have contributed to the chloride profile, and also because it does not give an instantaneous measure of the current resistance to chloride penetration. Instead it yields the ‘time-averaged’ performance of the concrete, over the period between first exposure of the structure and the time when the chloride profile was determined.

For both existing and new concrete structures a necessary component of any prediction of service life is an accurate estimate of the current (and future) resistance to deleterious substances. For concrete exposed to chloride ions, the service life is often taken to be the initiation period, which is the length of time necessary for the concentration of chloride ions at the depth of the reinforcement to exceed some threshold level considered sufficient to trigger the onset of active corrosion. As first noted by Collepardi, it is simple, at least in theory, to use Crank’s solution to calculate this initiation period once a structure is classified by its environment (a $C_s$ value) and by the quality of the constituent concrete (a $D$ value).

1.3 Time-Dependent Diffusivity

Extensive observations of marine structures in Japan lead Takewaka et al to propose that equation (1) requires modification allowing for an apparent temporal (time related) dependence of the diffusion coefficient. That is, the resistance of concrete to chloride ions, as determined by ingress profiles, is seen to improve with age according to a simple power function:
\[ D_{\text{eff}} = D_{\text{eff}0} \times \left( \frac{t_0}{t} \right)^m \]  

(2)

where \( D_{\text{eff}0} \) is a known diffusion measurement made at some reference time \( t_0 \) (usually chosen so that \( t_0 = 1 \) in the time scale used) and \( m \) is an index quantifying the reduction in diffusivity. Maage et al.\(^8\) and Mangat et al.\(^9\) among others have confirmed this relationship appears to hold for both laboratory specimens and aged concrete in the field.

Under this model, values of \( m \) that make physical sense are in the range 0, signifying constant diffusivity with time, to 1, which implies the concrete has becomes blocked to further chloride ingress. The later situation has been reported for some very low water/binder ratio concretes incorporating supplementary cementitious materials\(^{10}\). The value of \( m \) is dependent on (at least) cement type and water/binder ratio. Data published by Bamforth\(^1\) and Maage et al.\(^8\) indicate that concrete incorporating blast-furnace slag, fly ash or silica fume show substantial reductions in effective diffusivity corresponding to \( m \) values of approximately 0.6 – 0.8. Plain Portland cement concretes show much smaller reductions; Bamforth\(^1\) indicates an \( m \) value of 0.25 while Takewaka’s\(^7\) original figure was \( m = 0.1 \).

1.4 Unanswered Questions

The implication of \( D_{\text{eff}} \) decreasing with time is that any prediction of the long-term chloride concentrations developed in a concrete structure by applying equation (1) with a \( D_{\text{eff}} \) value measured at an early age will overestimate those concentrations. Therefore a service life prediction model that does not include an allowance for time dependent diffusivity will give overly conservative estimates of the durability performance of concrete types found to possess large \( m \) values (reduction indices). However, there are a number of problematic issues that hinder the confident adoption of this concept in service life design and prediction methodologies.

For example, no conclusive explanation for this phenomenon has been advanced. Given that the underlying control on all chloride transport is the distribution and continuity of pores within the concrete, most justifications for reduced diffusivity invoke the possibility of continued hydration and pozzolanic reactions and/or the precipitation of insoluble salts at the concrete surface. If this is the cause, it seems probable that the potential for improvement is finite and also to some degree dependent on environment. Assuming an ongoing improvement with time may therefore be presumptuous.

Furthermore, the relationship between \( D_{\text{act}} \) and \( D_{\text{eff}} \) is unclear. While only effective diffusivity is ultimately important for service life, it would be useful if a relationship between \( D_{\text{eff}} \) and \( D_{\text{act}} \) could be derived. Actual diffusivity is a material parameter of the concrete that is easily determined in the laboratory at the time of construction. In comparison, \( D_{\text{eff}} \) can only be determined ‘after the fact’ from field measurements or by analogy with existing concrete in a similar environment. Such historical information on the performance of a particular concrete may not be available at the design stage.

Existing information on the relationship between the two different diffusivity determinations is somewhat contradictory. Maage et al.\(^8\) present data that suggests \( D_{\text{act}} = D_{\text{eff}} \) shortly after exposure and that the ratio \( D_{\text{eff}}(t) / D_{\text{act}}(t) \) at any particular time decreases with age in a predictable way. Mathematically if the temporal reduction in
effective diffusivity solely reflects a genuine improvement in the intrinsic resistance of the concrete to chloride diffusion then:

\[
D_{\text{eff}} = \frac{1}{t - t_{\text{ex}}} \int D_{\text{act}}(u) du
\]  

That is, the effective diffusion coefficient is the mean value of the actual diffusion coefficient over the period between the initial exposure to the chloride-laden environment and the final determination of the chloride ingress profile.

2. Experimental Programme

In an attempt to clarify some of these issues BRANZ placed a series of thirty-six 1.0 m x 0.75 m x 0.35 m structural concrete blocks on three exposure sites in late 1998. The sites were chosen to be representative of typical New Zealand marine exposure environments of varying severity. This paper deals exclusively with concrete samples placed at Weka Bay, a small bay within the confines of Wellington Harbour. The specimens are placed, cast face uppermost, approximately 0.5 m above the high water mark. Thus they are never submerged but experience repeated cycles of wetting and drying due to wave action. This was considered to be an example of the most aggressive conditions for chloride ingress.

Mix details are summarised in Table One. Concretes were produced with 325 and 400 kg/m\(^3\) total cementitous material and consisted of control mixes with Portland cement and reference mixes incorporating blastfurnace slag, silica fume and a natural amorphous silica. Further details of the mixes and other exposure sites in the programme are available in Chisholm and Lee.

Chloride penetration has been monitored for each of the concrete mix types by measuring the total chloride concentration at 3 mm depth increments below the exposed face. A minimum of seven increments were used to define each ingress profile; if the chloride concentration of the deepest increment exceeded 0.05\% by mass of concrete, further increments were added to improve resolution. To date profiles have been taken after 6, 12, 18 and 30 months’ exposure. This information has been used to calculate effective diffusivities for each of the concrete types by modelling the fit of equation (1) as previously described. To accompany the determination of \(D_{\text{eff}}\), the interior concrete from 100 to 150 mm below the surface was sampled by coring to monitor any changes in \(D_{\text{act}}\), the actual diffusivity of each concrete. This was determined using a method equivalent to NT Build 443.

3. Results

The calculated effective diffusion coefficients for each of the concrete types are presented in Table Two, together with a calculated value for the reduction index \(m\). This is found according to equation (2) by plotting \(D_{\text{eff}}\) vs. time in a double logarithmic coordinate system; the slope of best-fit linear trend line equals negative \(m\). Examples for a few of the concrete mixes are shown in Figure One. The results show a small reduction in the diffusivity of the slag concretes \((m = 0.27\) and 0.36\) which is significantly less than that previously reported. In contrast with Maage et al the silica fume concretes show no evidence of a time-dependent \(D_{\text{eff}}\). The data for Portland cement concrete and concrete containing the natural amorphous silica is contradictory, with two of the concretes from each mix type producing negative \(m\) values. This
signifies that the effective diffusivity over the first 30 months exposure has, on average, increased with time.

Measurements of the actual diffusivity of the concretes are given in Table Three. Currently data is only available for the 400 kg/m³ mixes up to 18 months. \(D_{\text{eff}}\) for the slag concretes show a small decrease with time, paralleling the trend of their \(D_{\text{eff}}\) values. The actual diffusivity of the other concrete mix types appears to be constant.

4. Discussion

According to the time-dependent diffusivity model, the speed with which chloride increases at depth in concrete is very sensitive to the value of \(m\). This is demonstrated in Figure Two, which shows the chloride build-up through time for a hypothetical concrete with an early age (28 day) diffusion coefficient of \(5 \times 10^{-12} \text{ m}^2/\text{s}\), experiencing a typical marine tidal / splash zone surface chloride load of 2.5% by mass of cement. The three plotted curves give the chloride concentration at a typical cover depth of 50 mm for \(m = 0\) (constant diffusivity with time), \(m = 0.3\) and \(m = 0.5\). If the commonly accepted corrosion threshold value of 0.4% is accepted, the safe period before rebar corrosion can occur is approximately 5 years, 20 years, and far greater than 100 years for the three cases respectively. This effect far outweighs the benefit of optimising early age diffusivity. Without allowing a temporal reduction in \(D_{\text{eff}}\) it is necessary to reduce the initial diffusion coefficient of the concrete in the example by a factor of five to achieve an initiation time of 20 years. This is illustrated by the dotted line in figure two.

Given the sensitivity of achieved performance to the time reduction index, \(m\), relying on a prediction model that incorporates time-dependent diffusivity for concrete specification purposes requires considerable confidence that the magnitude of the projected improvement is correct. In this light, it is interesting to consider why the concretes on the Weka Bay site might show weaker evidence of time-dependent diffusivity than reported by other authors, and to speculate on alternative explanations for apparent time-dependence. A number of possibilities can be proposed:

**Misinterpretation of a change in the predominant transport mechanism with temporal dependence:** A difficulty with trying to study diffusion coefficients is the power-law nature of equation (2), which means the greatest change in \(D_{\text{eff}}\) occurs very early in the exposure history of the concrete. Figure Three is an illustration of this; it shows how \(D_{\text{eff}}\) is expected to change for 0.45 w/b ratio Portland cement and slag concretes based on data from Bamforth. Clearly, the magnitude of change before six months is far greater than the change from six months onwards. For profiles measured later than six months, there is an increased risk that any discernable trend in the diffusivity will be masked by variations in the chloride ingress due to other factors. The high scatter in figure one is evidence of this problem.

In order to maximise the confidence with which \(m\) can be determined, measurements of reduction in \(D_{\text{eff}}\) frequently include profiles determined as early as possible, even after as little as seven days exposure, e.g. 8. This is an acceptable practice where concrete is saturated until the time of exposure and completely submerged in seawater thereafter. For situations where the concrete is exposed intermittently to chlorides and subject to wetting and drying cycles, this is potentially a source of error. As previously noted, \(D_{\text{eff}}\) is a ‘bundled’ parameter that measures the combined effect of all possible chloride transport mechanisms without distinction. It seems reasonable that for concrete
that is only infrequently splashed by waves initial ingress is dominated by absorption
due to capillary action, as relatively dry near-surface pores are wetted by chloride
solutions. However, once a concentration is established in this zone, and at greater
depths where the pores are more likely to be saturated, diffusion will play a far greater
role. A numerical simulation of chloride transport in non-saturated concrete indicates
that absorption gives rise to more rapid ingress than diffusion. This one-off transition in
transport mechanisms (from absorption to diffusion) would appear as a temporal
improvement in $D_{eff}$. Extrapolating this short-term behaviour of $D_{eff}$ over the projected
life of a concrete structure risks an unduly optimistic assessment of potential life.
Absorption will have a bearing on the chloride profiles from the Weka Bay blocks, but
the effect on the calculated change in effective diffusivity will be less apparent than if
there was a sampling history before six months’ exposure.

**Lack of similarity between laboratory studies and the Weka Bay field environment:**
Because of this interference by multiple transport mechanisms, the majority of
laboratory measurements cited as evidence for a reducing diffusivity have been made
under the readily reproducible conditions of saturated samples continuously immersed
in seawater e.g. 8,15. Constant submergence of concrete represents ideal conditions for
the improvement of intrinsic diffusion. The water necessary for continued hydration to
refine the capillary pore structure is readily available. Moreover reaction products such
as magnesium hydroxide and calcium carbonate formed by ion exchange with seawater
can significantly reduce the permeability of the concrete’s skin. Optimum hydration
and self-sealing reactions are less likely to develop where the concrete is exposed to
repeated wetting and drying cycles as at Weka Bay. As an aside, a completely
submerged section of reinforced concrete is in a relatively benign corrosion
environment because the availability of oxygen is typically low.

Evidence of significant continued hydration should be apparent by a reduction in actual
diffusivity. This should be easier to detect than changes in $D_{eff}$. Following the
mathematics of equation (3) $D_{act}$, an ‘instantaneous’ measurement, will decrease more
rapidly than the time-averaged $D_{eff}$ value it controls. The determination of the reduction
index can also be made more precisely because the test specimens are completely
saturated and so can be carried out reliably at earlier ages. For the 400 kg/m$^3$ slag
concrete, the observed improvement in $D_{eff}$ implies that the change in actual diffusivity
would need to give a reduction index of $m = 0.48$ to account for the magnitude of the
reduction. The calculated $m$ value is, in fact, 0.21 (table two). This appears to indicate
that continued hydration cannot be the sole contributor to the noted reduction in
effective diffusivity.

**Misinterpretation of a spatial dependence as an apparent temporal dependence:** While
$D_{eff}$ is often assumed to be a function only of time, it is probable that it is also spatially
dependent. The exposed surface of most field concrete is likely to have a diffusion
coefficient significantly different to that of its interior. For example, Higgins has
shown that the cement to aggregate ratio is much higher in the top 10 mm from a cast
face than the bulk of the concrete. The surface is also likely to be less well-cured, and
carbonated thereby reducing chloride binding ability, and to have percolated interfacial
transition zones directly in contact with the environment. All these factors serve to
increase diffusivity. Computer simulations by Bentz et al. have demonstrated that if the
diffusivity of the surface concrete exceeds that of the interior, conventional Fick’s Law
analysis will predict a power law type behaviour for $D_{eff}$ with time even when no such
relationship actually exists. This arises from the fact that the higher diffusivity outer layer is 'sampled' earlier in time than the bulk concrete. In the case of the Weka Bay blocks the sampling may still be too early and too shallow to be sensitive to this transition, i.e. the chloride profiles are still largely within the surface layer.

Unwarranted assumptions in assessing the performance of older field structures: An alternative to the uncertainties of projecting long-term behaviour from early trends is examining the historical performance of particular concrete type if a suitably lengthy service history is available. However this often involves making assumptions to enable past and present diffusion coefficients to be calculated. Estimation of long-term changes in $D_{\text{eff}}$ values for older slag concrete structures given in an influential paper by Bamforth was based on crack formation being observed shortly after the initiation of reinforcement corrosion. This assumption of a negligible propagation period may not be justifiable for concrete containing supplementary cementitious materials; their high resistivity will limit the extent of anodic areas on the reinforcement, slowing the corrosion rate. Thus the duration of the initiation period relative to the propagation phase may have been over-estimated, exaggerating the apparent reduction in $D_{\text{eff}}$.

5. Conclusions
Of the four concrete types examined, only concrete incorporating blast-furnace slag has shown an apparent improvement in resistance to chloride ingress after 30 months’ exposure on a marine splash-zone site. The reduction in diffusivity observed for the slag concrete has been less than prior studies suggest could be expected. While this is insufficient to refute the well-established concept of a temporal dependence in chloride ion diffusivity, it illustrates that the mathematics of empirical models of this phenomenon should not be too rigidly relied on. This is particularly the case given that the exact mechanism behind the improvement, and the conditions under which it can be confidently expected to occur, are yet to be adequately explained. Service life prediction models that incorporate this theory should be treated with a degree of caution, and $m$ values should be chosen to be conservative, particularly if cover is traded for a projected improvement in concrete performance. Specification of durable concrete should focus upon optimisation of desirable properties like intrinsic chloride diffusion and capillary absorption that can be demonstrated by early-age characterisation testing.

6. Acknowledgement
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7. References


7 Takewaka K. and Mastumoto S. ‘Quality and Cover Thickness of Concrete Based on the Estimation of Chloride Penetration in Marine Environment’ in ACI SP 109, Detroit, 1988.


12 Poulsen E. ‘Four-Parametric Description of Marine Exposure and Concrete’s Response to it’s Chloride Intensity’ in ‘Proceedings of the International Conference Repair of Concrete Structures – From Theory to Practice in the Marine Environment’, Norwegian Road Research Laboratory, 1997, pp 89 – 199.


Concrete Mixes

| 19mm crushed greywacke (kg) | 763 | 761 | 764 | 764 | 761 | 763 | 765 | 759 |
| 13mm crushed greywacke (kg) | 326 | 320 | 325 | 318 | 320 | 317 | 319 | 322 |
| Manufactured sand (kg) | 844 | 778 | 846 | 781 | 842 | 803 | 832 | 749 |
| GP Cement GP (kg) | 326 | 399 | 302 | 370 | 306 | 373 | 45 | 50 |
| Slag cement (kg) (75% slag) | * | * | * | * | * | * | 279 | 350 |
| Natural Amorphous Silica (kg) | * | * | * | * | 26 | 32 | * | * |
| Silica fume (kg) | * | * | 26 | 32 | * | * | * | * |
| Total Cementitious (kg) | 326 | 399 | 328 | 402 | 332 | 405 | 324 | 400 |
| Super Plasticizer (l) | * | * | 2.7 | 3 | 0.6 | 2.5 | 1.6 | 0.6 |
| Total Water (l) | 159 | 160 | 159 | 183 | 169 | 157 | 160 | 175 |
| Slump After SP (mm) | * | * | 100 | 100 | 100 | 150 | 110 | 100 |
| Fresh Density (kg/m³) | 2403 | 2421 | 2419 | 2406 | 2403 | 2434 | 2442 | 2442 |
| W/B ratio | 0.49 | 0.40 | 0.51 | 0.45 | 0.51 | 0.39 | 0.49 | 0.44 |

Table One: Concrete mix details. Quantities per m³

<table>
<thead>
<tr>
<th>Concrete Type</th>
<th>Cementitious Material (kg/m³)</th>
<th>Effective Chloride Diffusivity, $D_{eff}$ ($10^{-12}$ m²/s)</th>
<th>Reduction Index $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement Control</td>
<td>325</td>
<td>2.67</td>
<td>4.49</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.44</td>
<td>2.52</td>
</tr>
<tr>
<td>Slag Cement (75% slag)</td>
<td>325</td>
<td>1.30</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.26</td>
<td>0.77</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>325</td>
<td>0.87</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.06</td>
<td>0.72</td>
</tr>
<tr>
<td>Natural Silica</td>
<td>325</td>
<td>1.28</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.40</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table Two: Mean effective diffusion coefficients

<table>
<thead>
<tr>
<th>Concrete Type</th>
<th>Actual Chloride Diffusivity, $D_{act}$ ($10^{-12}$ m²/s)</th>
<th>Reduction Index $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement</td>
<td>12.1</td>
<td>10.4</td>
</tr>
<tr>
<td>Slag Cement (75% slag)</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>5.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Natural Silica</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table Three: Mean actual diffusion coefficients
Figure One: Example of fitting of 'm' values to measured effective diffusion coefficients

\[ y = -0.3596x - 0.0347 \]

\[ y = 0.2623x + 0.2767 \]

\[ y = -0.1603x - 0.4363 \]

![Graph showing fitting of 'm' values to measured effective diffusion coefficients](image)

Figure Two: Illustration of effect of reduction index 'm' on chloride concentration at 50 mm cover

![Graph showing effect of reduction index 'm' on chloride concentration](image)

Figure Three: Example of expected hypothetical reduction variation of effective diffusivity based on power law

![Graph showing variation of effective diffusivity based on power law](image)