Modelling Durability of Concrete Below Ground

Norwood Harrison¹, Daksh Baweja² and <u>Peter Sleep</u>³ ¹Concrete Pipe Association of Australasia ²BG&E Materials Technology ³Humes, Holcim Australia

Abstract: Natural agents potentially aggressive to concrete below ground include acids, dissolved carbon dioxide, sulfates and chlorides.

Experimental data derived from samples immersed in acid solutions of controlled pH, supplemented by field observations, have provided relationships giving depth of attack as a function of exposure time and the concentration of aggressive agent, together with appropriate allowance for the effect of soil type. Using relevant data from literature the analysis is extended to aggressive CO₂. Long-term performance (up to 24 years) of samples immersed in sulfate solutions has confirmed that low w/b is able by itself to provide very high resistance to sulfate, though the results also suggest a further benefit from SCM in the binder. For exposure to chloride, the diffusion coefficient is the same whether the boundary condition is expressed as a concentration of chloride in the concrete, or in moisture at the concrete surface, enabling data obtained from above-ground marine exposure to be adapted to conditions underground.

This information is consistent with specifications in the concrete pipe Standard AS/NZS 4058, with the possible exception of exposure to high levels of sulfate, for which a requirement appears to be justified for the use of blended cement.

Keywords: concrete, acid, carbon dioxide, sulfate, chloride.

1. Introduction

To date, much of the emphasis on modelling deterioration of concrete structures has applied to above ground exposure, with effects resulting from carbonation or diffusion of chloride (1). From the early 1970s the pipe industry has assembled data relating to conditions underground, supplementing empirical data from literature with long-term tests carried out under laboratory conditions, and examples from the field. In this paper, details of both experimental investigations and measurements from field-exposed concrete are presented, providing quantitative data relating in particular to rates of attack from exposure to acid (low pH) and aggressive carbon dioxide dissolved in groundwater. Experimental data from exposure to sulfate is also presented, together with conclusions which may be drawn from literature concerning the effect of chloride.

While the detail applies to exposure conditions and physical structure of buried concrete pipes, some of this can be extended to other types of structure. However such application should be limited to structures entirely below ground, with concrete having water/binder ratio no greater than 0.4.

The data presented underline the specifications in AS/NZS 4058 and will support the review of that Standard, when it becomes due.

2. Experimental Series

The experimental series described in this paper were initiated in the early 1970s. At that time general accounts of concrete durability, including conditions below ground, were available in textbooks (2, 3), together with examples in individual publications. These included effects on high quality concrete as used in pipes, but without enough detail to set representative rates of attack by acid or aggressive carbon dioxide, or reasonable limits for the concentration of sulfate. The experimental series were initiated to provide these details, including the effect of changes to concrete mix designs being considered at the time.

2.1 Method

Test samples were cut from non-reinforced spun pipe which had been given a brief steam curing cycle (3 hours total) prior to demoulding, followed by "air curing" for 3-8 weeks. The materials employed were:

Portland cement - Geelong ARC

- Conforming to AS A2-1963, type "normal".
- Likely to be similar to Type GP as described in AS 3972-2010, with no mineral addition. Particle size distribution may differ from typical present-day material.

Sulfate resisting (Portland) cement - Gippsland R

- Conforming to AS A2-1963, type "sulfate resisting".
- Likely to be similar to Type SR as described in AS 3972-2010, with no mineral addition. Particle size distribution may differ from typical present-day material.

Fly ash - commercial supply by Pozzolanic, Queensland

- Conforming to AS 1129-1971.
- Likely to be similar to Grade 1 fly ash described in AS 3582.1-2016 and Fine Grade fly ash described in AS 3582.1-1998.

Basalt coarse aggregate (10 mm)

• Conforming to AS A24.

• Likely to conform to provisions of AS 2758.1-1998.

Silica sand

- Conforming to AS A24.
- Likely to conform to provisions of AS 2758.1-1998.

Notwithstanding differences in definitions and terminology between AS A2 and AS 3972, the two Portland cement types will be referred to here as GP and SR, respectively, for Geelong ARC and Gippsland R. Binder in the test concrete consisted of one or other of the straight Portland cements, or a blend with fly ash. For concrete made without fly ash the cement content was 400 kg/m², while with fly ash blends the binder was 330 kg/m³, with 20% fly ash. The spinning process typically results in free water 130 L/m³ at the end of the spinning cycle, which translates to w/b 0.33 and 0.39, respectively, for the two levels of binder.

Test samples were beams of nominal dimensions 50x50x300 mm cut from the pipes in the axial direction. Exposure to test solutions consisted of full immersion at ambient temperature in Melbourne where the work was carried out. It was clear at an early stage of testing that changes in weight and dimensions of the samples would not provide any worthwhile assessment of deterioration, and the principal measure adopted was flexural strength. The series included control samples immersed in water, free of any aggressive component, to represent ongoing curing.

2.2 Exposure to pH levels potentially aggressive to concrete

In this series the binder consisted of GP cement or a blend of GP with fly ash.

In choosing the severity of exposure, levels of pH were selected to represent a potentially aggressive condition within the range likely to be encountered in the field, and a lower (more aggressive) level, with the aim of obtaining accelerated results – respectively pH 5.0 and pH 3.5. A textbook buffered solution derived from the work of Walpole (4) was chosen for the exposure, consisting of sodium acetate at a concentration of 0.2 moles per litre, with addition of hydrochloric acid to give the required level of pH. Acid attack progresses from the surface, leaving a layer of low-solubility products of reaction which if undisturbed have the effect of slowing further attack (5). The effectiveness of this layer in slowing further attack is influenced to some extent by solubility of calcium salts formed from the acid and calcium in the cement, which if soluble can diffuse out over time giving greater access to the unaffected concrete. Chloride and acetate salts of calcium formed by reaction with cement of the solution type chosen for this investigation are water soluble and so will have the least effect in inhibiting the rate of attack.

The exposure at pH 3.5 ran for five years, with regular testing of the solution and correction of pH throughout that time. With the series at pH 5.0, regular checks and corrections were made up to nine years, but from that time the solution and immersed samples were left undisturbed until the exposure was concluded at 24 years, at which time the pH had risen to 5.9.

Under the circumstances of these tests, the attack resulted in a distinct change in the appearance of the concrete, visible at a fractured surface as shown in Figure 1. On the reasonable assumption that the affected concrete has little remaining strength, the loss of strength of beams immersed in a test solution, compared with those in water at the same age, directly reflects the depth of attack, which may then be

calculated using the standard relationship from Roark (6) between material strength and the load or bending moment which a beam can support.



Figure 1. Fractured surfaces of test beams – pH 5.0, 24 years

Flexural strength of beams immersed in water, and in the solution at pH 5.0, are shown in Figure 2. In water, the strength continued to increase even beyond a year. Samples in the solution at pH 5.0 increased in strength up to about three months due to ongoing curing, but at longer times showed progressive loss as a result of attack by the acid.



Figure 2. Strength progression of test samples in water and at pH 5.0

Test data shown in Figure 2, and for the further series of exposure at pH 3.5, have been analysed as described above to provide depths of attack from the relative strength values obtained for immersion in the aggressive solution and in water. For reference, the adopted formula is:

$$d = B[1 - (f_2/f_1)^{\frac{1}{3}}]/2$$

(1)

in which d is the depth of attack, f_1 and f_2 are the mean flexural strengths calculated from original dimensions, for immersion in water and the test solution respectively; and B is the nominal side dimension of the beam cross section. Depths of attack calculated in this way are shown in Figure 3

The spread of plotted points for the GP (Portland cement only) mix and fly ash blend indicate in each instance that a single trendline is appropriate to represent both binder types. In selecting the algebraic form of trendline the first option considered was an equation of the form

$d = kt^n$

analogous to that used for carbonation, for which the exponent $n = \frac{1}{2}$. It was found however that a better fit to the trendline (ie lesser sum of squares of residuals) was obtained with n less than $\frac{1}{2}$. Values for k and n giving the best fit to data were then determined separately for the exposures to pH 3.5 and 5.0. With log (depth) plotted against log (time) Equation 2 gives a straight line. It was found however that with relationships of the form

$$d = m x \log(t) + b$$

(3)

(2)

in which m and b are constants, lower values for sum of squares were obtained than the best corresponding to Equation 2, and also better correlation (measured by the Pearson function) between the two variables. Values from the analysis are shown in Table 1.



Figure 3. Depth of attack after exposure to acid

Fable 1. Bes	st fit of data	a to Equation	n 2 and Equation 3
--------------	----------------	---------------	--------------------

Relationship	pH 3.5		pH 5.0	
	Sum of squares ¹	Coefft of correlation	Sum of squares	Coefft of correlation
Equation 2	32.8	0.853	16.9	0.834
Equation 3	20.1	0.911	13.4	0.869

- 1. Unit of length millimetres.
- For trendlines following Eqn. 2, least sum of squares were obtained with n = 1/3.1 for pH 3.5, and n = 1/3.4 for pH 5.0.
- 3. To allow for the higher pH found at the end of the exposure period at nominal pH 5.0, the trendline is calculated with age set at 12 years for the last strength values.

Trendlines shown in Figure 3 are best fit to the log-linear relationship, Equation 3, with parameters as shown in Equations 4 and 5.

For pH 3.5,	
$d = 4.187 \times \log_{10}(t) + 5.32$	(4)
and for pH 5.0,	
$d = 2.446 \times \log_{10}(t) + 3.17$	(5)

in which depth d is in millimetres and time t is in years.

For the dependence on pH, consideration must be given to the chemical "law of mass action", according to which the rate of a chemical reaction is proportional to concentrations of the reactants. Observed rates may not always comply with this relationship but it may be taken as an initial assumption. Equation B1.1-2 of fib Bulletin 34 (7), setting the rate of carbonation, is an example of the application of this law. pH is a reversed logarithmic scale of concentration of the active component of acid, the hydrogen ion, whose concentration is then proportional to $10^{(-pH)}$, increasing by a factor of 10 for each unit reduction in the pH value. The law of mass action then predicts a corresponding change in the time scale of its effect.

This relationship enables Equation 3 to be extended to include dependence of depth of attack on pH as well as time. If T is the time variable at the pH value pH_0 applicable for parameters m and b, then changing to time variable t in which

$t = T \times 10^{(pH-pH_0)},$	(6)
$T = t \times 10^{(pH_0-pH)}$ and	(7)
$d = m \times \log [t \times 10^{(pH_0-pH)}] + b$ or	(8)
$d = m x [log(t) + pH_0 - pH] + b$	(9)

showing a linear relationship between depth and pH for any nominated period of exposure. Equation 9 can be used to calculate d using values of m and b from either Equation 4 or Equation 5, for any chosen time of exposure. Predicted depths at 100 years from the two series are shown in Table 2.

Table 2. 100-year depths from experimental series

Values m and b	100-year depth (Equation 9) at pH		
from	3.5	5.0	
Equation 4	13.7	7.4	
Equation 5	11.7	8.1	

Considering that exposures in the two experimental series were entirely independent, the depths at the two levels of pH represented in Table 2 are in close agreement and it is reasonable to use the average in each case as a representative value. Equation 9 contains two constant terms m x pH₀ and b, which together with m x [log(t)-pH] define the relationship between depth, pH and time. Expressed in the generic form of linear relationship defined by parameters m and b, Equation 9 becomes

$$d = b - m \times [pH-log(t)]$$

in which **m** and **b** are shown in bold to distinguish them from the m and b of Equation 3, and the order of terms is reversed to avoid a negative coefficient. Values for **m** and **b** can be determined by solving for the average 100-year depths at pH 3.5 and at pH 5.0 from Table 2, giving

(10)

(11)

$$d = 17.7 - 3.317 x [pH-log(t)]$$

where exposure time t is in years and depth of attack d is in millimetres. Equation 11 is the outcome sought from this experimental series.

2.3 Exposure to sulfate

The experimental series included immersion of samples as described in Section 2.1 above in solutions of sodium sulfate. Test concentrations were chosen, using the accounts in textbooks available at the time (3, 8), to represent a low level which could nonetheless affect susceptible types of concrete, and a higher concentration beyond which natural occurrence would be extremely rare. The two levels chosen were 2000 and 10,000 ppm SO₄. Test beams were withdrawn progressively and broken in flexure, as for the immersion in acid. Sulfate exposure at 2000 ppm continued for five years, and at 10,000 ppm for 24 years. Regular checks and corrections were made to the solutions and the final analysis at 24 years showed the correct levels of sulfate.

For this series parallel sets of samples were exposed in which the Portland cement component was Geelong ARC (GP) or Gippsland R (SR). While the composition of Geelong ARC did not meet the prescription of the time for classification as sulfate resisting, its chemical make-up would nonetheless have provided a high level of resistance to sulfate, and it would probably qualify as sulfate resisting in accordance with AS 3972-2010. In both 2000 and 10,000 ppm sulfate levels strength of beams continued to increase beyond a year, having similar values to those immersed just in water, and there was no loss of strength with continuing immersion up to four years. In the 2000 ppm series there was no loss of strength at the conclusion of the series, after five years' immersion.

In the series at 10,000 ppm, a sample with SR binder (no fly ash), tested after 9 years, showed a small loss of strength compared with previous examples, and further confirmation of deterioration in the absence of fly ash was provided by a visual inspection at 16 years, in which a sample made with GP had become visibly bent and cracked. From that time the remaining samples immersed in sulfate at 10,000 ppm consisted of the single GP, two with SR (no fly ash) and two with SR fly ash blend, all of which were tested at 24 years. The samples with fly ash did not exhibit any loss of strength, whereas GP

and SR (Portland only) were severely weakened. Results from immersion at 10,000 ppm sulfate are shown in Figure 4.



Figure 4. Strength after exposure to 10,000 ppm sulfate

It is consistent with results from this series that while the composition of some Portland cements will predispose them to resist sulfate attack, in high levels of sulfate the binder must contain SCM in order to prevent deterioration after a long period of exposure.

3. Estimation of in-ground rates of attack

While the experimental series give indications of rates to be expected in conditions of exposure resembling those adopted for the measurements, to assess in-ground conditions these must be supplemented by observations representing the much wider range of conditions which apply in the field. In this section field examples are presented of effects of acid and aggressive CO₂, while results for sulfate are compared with previously compiled data of this kind.

3.1 Action of aggressive CO₂

Natural waters including groundwater often contain concentrations of dissolved carbon dioxide well above the level corresponding to equilibrium with CO_2 in the atmosphere. Large quantities of CO_2 can be released by decomposing organic substances (3) but in many, if not most instances the source of dissolved CO_2 is unknown. Water containing dissolved CO_2 is able to dissolve calcium, from cement or other sources of this element (such as calcium carbonate), provided there is a surplus to hold the calcium in solution as bicarbonate. If the water is already "hard", containing calcium or magnesium as bicarbonate, only part of the remaining uncombined or "free" CO_2 is available to dissolve a larger amount of calcium, the remainder being required to stabilise the bicarbonate already in solution. This surplus comprises the component aggressive to concrete. Lea (2, p 340) sets out a method for estimating the aggressive component from the free CO_2 and the amount of calcium originally dissolved in the water.

Literature (2, 5) reports significant aggressiveness at concentrations in the range 15-30 ppm. While dissolved CO_2 reduces pH, even with small amounts of dissolved calcium the pH is increased to levels which alone would be harmless to concrete, while the surplus CO_2 component remains aggressive in its own right. Taking an example from Lea (2, p 341), a solution having 28 ppm CaO equivalent of dissolved calcium and 27 ppm of CO_2 above the level required to stabilise the calcium in solution, exhibits pH 6.7. On the basis of pH alone, without regard to CO_2 component, this water would be wrongly assessed as non-aggressive to concrete. While attack by aggressive CO_2 proceeds in essentially the same way as with acid, by dissolution of calcium from the cement, separate assessment is required of its effect.

3.2 Acid and aggressive CO₂ – rates of attack

With acid the active component is the hydrogen ion, which converts the calcium to a salt of the acid type present; with aggressive CO_2 calcium is dissolved as bicarbonate. Thus a correspondence can be expected between concentrations of aggressive CO_2 , and pH where there is no CO_2 present. Literature does not provide this correspondence directly; however in the traditional accounts of effects of aggressive CO_2 on concrete (2, 3) a level of 15 ppm is shown as a threshold above which there will be some effect on

concrete, which would correspond to about pH 5.5 for the hydrogen ion. The similarity continues at higher concentrations at the same molar ratio (which turns out to be 100/1, CO_2/H^+), where pH 5.0 and 50 ppm of CO_2 are both "significantly" aggressive, enabling the relationships developed for pH to be adapted for aggressive CO_2 .

Examples available from a range of sources in addition to the experimental series described in Section 2 above, cover the range pH 3.5 to 5.9, for durations of exposure 3 to 30 years; or aggressive CO_2 7 to 121 ppm, with exposures 2 to 27 years. To enable the results to be shown graphically in a form relevant to design, depths recorded in these examples have been extrapolated to 100 years using the time dependence represented by Equation 11. Results are shown in Figure 5, together with relationships derived from analysis set out previously (Section 2.2) and the correspondence between pH and aggressive CO_2 , shown as reference lines. The line shown in Figure 5 (a) is a plot of Equation 11. In Figure 5 (b) the appearance of the reference line differs from that in Figure 5 (a) because the horizontal axis has a linear scale of increasing concentration, whereas the scale of pH in Figure 5 (a) is equal to the logarithm of concentration reversed in direction by a negative sign. However depths of attack are the same in both figures, for concentrations in the molar ratio giving the same rates of attack.



Figure 5. Depth of attack after 100 years. (a) acid, (b) aggressive CO₂.

In Figure 5 (a) examples 1 to 8 are from field observations of installed pipes, showing the depth of attack of surfaces in contact with the soil. With the exception of no. 2, for which there was also aggressive carbon dioxide in the groundwater, these lie comfortably below the reference line. Nos. 9 and 10 are from a long-term (22-year) experiment conducted under laboratory conditions (9) in which a large container was filled with coarse gravel and water of controlled low pH, kept in slow circulation through the gravel. Figure 5 (a) shows as nos. 9 and 10 respectively samples immersed directly in the gravel, or surrounded by a layer of clay "backfill" also in contact with the circulating liquid. The effect of the clay backfill can be read off the graph as an equivalent change in pH, from the interval between the point and the reference line at the same depth – in this case an increase of somewhat more than one unit of pH. Positions of the other plotted points referring to external attack can be interpreted similarly, their lower position relative to the reference line being due to restricted movement of water allowing the concrete to increase the pH at its surface, or simply absence of groundwater through part of the year. Further descriptions of the conditions and results pertaining to field examples are available through the Concrete Pipe Association of Australasia.

In examples 11 to 14 the exposure is to industrial waste (from food processing) passing through the pipeline. In the exposure condition from which the reference line is derived (ie immersion as described in Section 2.1) low pH solutions had direct access to the concrete surface, and so there is no ready explanation of the greater rates exhibited by these points. However from the plotted points it must be expected that for water flowing through a pipeline (inside), the reference line will underestimate the actual rate of attack.

Figure 5 (b) shows a similar pattern between the examples and the reference line, with examples relating to concrete in contact with the soil falling below the reference line, or seen as displaced in the direction of

a lower concentration of the aggressive. As with acid, exposure to liquid flowing through a pipeline can result in faster rates of attack than are indicated by the reference line.

3.3 Modelling based on observed rates of attack by acid and aggressive CO₂

Whereas effects of sulfate and chloride are significantly influenced by the type of binder, this does not appear to be the case with acids, including sulfuric acid formed by oxidation of pyrite in acid sulfate soils. At the concentration giving pH 3.5, a level of acidity highly aggressive to concrete, the sulfate component in sulfuric acid is a negligible 30 ppm. That Portland cements or the usual blends have similar resistance to acid is confirmed in the BRE Special Digest 1 (10), which allows any of the listed types for conditions primarily requiring resistance to acid. Similarly aggressive CO_2 does not discriminate between the different types of binder.

The reference lines in Figure 5 model rates of attack for concrete in contact with the soil, where there is groundwater present for a substantial part of each year, and the soil type allows free movement at the concrete surface. For heavy soils, the rate should be taken as that corresponding to one unit of pH higher than the reported value, or for CO_2 , lower concentration by an order of magnitude. Intermediate conditions should adopt half a unit of pH, or for CO_2 concentration reduced by a factor of three. It is not intended that the reference lines should be used directly for water flowing over a free concrete surface.

These reference lines can be readily compared with limits specified in AS/NZS 4058. For soil conditions giving ready access of groundwater to the concrete surface, the lower limit of pH allowed for the "normal" environment is pH 5.5, for which Figure 5 (a) shows attack to 6 mm depth in 100 years – well short of the required minimum cover of 10 mm. With the allowance as suggested above of one unit of pH for the least permeable soils this translates to pH 4.5, the limit in AS/NZS 4058 of the "normal" environment for this type of exposure. Similar considerations apply to aggressive CO₂, Figure 5 (b). These correspondences are no accident as the AS/NZS 4058 limits were set on the basis of experimental and field observations reported here, at an earlier stage in the investigations than were subsequently reached. The limits for the "normal" environment are in fact more conservative than indicated by these figures as the reinforcement will remain intact for a further period after the protection initially provided by the surrounding concrete has been neutralised.

3.4 Sulfate

Sulfate attack on concrete is covered in detail in the recently published Technical Note 68 from Cement Concrete & Aggregates Australia (11). The purpose of the discussion here is to integrate the information presented in that publication with the experimental findings of Section 2.3 above.

TN68 reports virtual immunity to sulfate levels in neutral and pH 3.5 conditions with concentrations far higher than the 10,000 ppm limit of the tests reported here, for concrete having w/b 0.4 and below, and with little effect from the type of binder. By contrast in these tests concrete having similarly low w/b and not containing SCM were affected by sulfate at 10,000 ppm after approximately ten years' immersion. The results may be no more than an aberration from more usual situations but even if confirmed are not a matter of any great practical consequence. Levels of sulfate from natural causes approaching 10,000 ppm sulfate are rare, if not unknown in Australia. While seawater contains about 3000 ppm sulfate, the effect is mitigated by the presence of chloride, which combines with the products of reaction between sulfate and hydrated cement to form water-soluble compounds which are unable to exert the disruptive effects which would otherwise occur. Cements whose chemical make-up predisposes them to sulfate attack should be avoided (5) but there is no need for compliance with Type SR. With sea water excluded, the limit of 1000 ppm sulfate set in the pipe Standard AS/NZS 4058 for binder which does not comply with type SR can be retained with very little inconvenience, but it would seem prudent to require the inclusion of SCM for exposure to sulfate above 3000 ppm (12).

TN68 has no mention of rates of attack by sulfate expressed as depth after a period of time. Sulfate resistance depends on appropriate choice of binder and a limit of w/b but there is no link to the required depth of cover to reinforcement. Similarly there is no concern about rates of replenishment at the concrete surface, with the consequent link to soil type, as with attack by acid or aggressive CO_2 . The latter are present in minute quantities - parts per million – and are consumed by the main constituents of the binder, the calcium silicates. By contrast significant concentrations of sulfate are orders of magnitude larger and only affect minor constituents of the binder. Thus a concrete surface is unlikely to have much effect on the concentration of sulfate which would otherwise be present, even where water movement is restricted by the type of soil.

3.5 Chloride

The effect of chloride penetrating concrete to reinforcing steel is perhaps the greatest area of concern for durability of concrete structures. Investigations have concentrated predominantly on direct exposure to sea water, and by contrast situations underground have been given relatively little attention. Unlike the treatment for other types of exposure SD1 (10), avoids recommendations for type of binder or w/b relating to chloride except as a consequence of its mitigating effect on sulfate (Section 3.4 above).

The most extensive and systematic investigation of chloride in above-ground structures has focussed on the diffusion process of chloride in concrete, with the point now reached where "typical or average" values for the diffusion property can be applied with some confidence, taking account of type of binder and w/b (1). Modelling design life requires a minimum of two further parameters, the surface concentration of chloride, and a threshold concentration at the steel deemed to signify the end of the design life or a recognised intermediate stage. The referenced publication Concrete Society Technical Report No. 61 (1) provides surface concentrations of chloride for conditions of marine exposure, to be used as typical average, or characteristically high values for this property. Concerning threshold levels for initiation of corrosion at the steel, TR61 referring to the work of Glass and Buenfeld (13) cites values varying from 0.25% to 2.5% of the binder (a tenfold difference), showing that there is unlikely to be a fixed value for a given concrete, while examples of even higher concentrations of chloride under conditions of above-ground marine exposure, with the steel unaffected by corrosion, may be found elsewhere (14). The threshold is best considered in terms of corrosion risk rather than any fundamental electrochemical property. TR61 comments further that the commonly used low values for the threshold appear to be most applicable in conditions of wet/dry cycling of high (>0.6) w/b mixes.

While reservations apply to adapting the research on marine exposure to situations below ground, there is no fundamental inconsistency in adopting the same values for the diffusion property. At the concrete surface, chloride not bound to the cement will seek an equilibrium concentration with groundwater, and the surface concentration of free chloride expressed as a mass percentage of the concrete (as used in diffusion calculations using the published values for the diffusion coefficient) is simply the concentration in the groundwater multiplied by the mass absorption ratio of water in the concrete. This figure could then be used in the diffusion calculation but a more consistent approach is to adopt the pore water concentration throughout – at the surface and at depth in the concrete. The diffusion coefficient remains the same.

As an example, concrete of the quality which is the subject of this paper will typically have absorption about 5% w/w. If the liquid at the surface has chloride 2% (similar to that in sea water), the concentration will be 2x0.05% = 0.1% w/w of the concrete, or for typical binder content round 400 kg/m³ and density 2,500 kg/m³, 0.6% of the binder. However in comparing concentrations in pore water with the Glass and Buenfeld limits one must allow for an assumed proportion of bound chloride, which from a related publication (15) may be taken as about 50% of the total chloride. With the above parameters this translates the upper limit of the Glass and Buenfeld range to 4% chloride in pore water. Corrosion observed under typical conditions of marine exposure is attributable to increased concentrations in pore water due to evaporation, and can be expected to correlate with average levels in the concrete only if similar conditions prevail overall.

The above considerations suggest that chloride up to 4% in groundwater will not cause corrosion of reinforcing steel. If higher concentrations are found then cover can be designed to limit the concentration in pore water adjacent to the steel to this value for the design life. The pipe Standard AS/NZS 4058 sets a more conservative limit of 2% chloride, which has not been found to cause inconvenience or unnecessary expense and there seems little point in adopting a higher value. Special Digest 1 (10) is cautious in its discussion of chloride but nominates an upper limit of concentration of 1.7% in its definition of "brackish" water and does not require any special type of binder or other protective measure for this type of exposure.

Where reinforcing steel is continuous through different conditions of exposure (for example both below and above ground) the steel potential in one location relative to the surrounding concrete can be influenced by effects elsewhere. If conditions above ground should allow the cathode reaction (combination of oxygen with water at the steel surface, releasing negatively charged hydroxyl ions) to proceed, the effect is to raise the potential of the steel, allowing the anode reaction (dissolution of the metal) to proceed elsewhere, even in the absence of oxygen where this is taking place. Thus a safe threshold for preventing corrosion of an isolated portion of reinforcement will not necessarily apply if there are steel bars or wires continuous across the ground level. No method is proposed here for dealing with this type of situation.

4. Conclusions

Investigations and analysis reported here apply to high strength concrete of the quality found in concrete pipes (w/b < 0.4), or of similar quality in other applications. Experimental data derived from samples immersed in acid solutions of controlled pH have provided relationships giving depth of attack due to acid as a function of exposure time and the concentration of aggressive. This has been extended to aggressive CO_2 (which acts similarly to acid but not at corresponding values of pH) using qualitative references in literature and field data. Both laboratory and field data have enabled appropriate allowance to be made for the effect of soil type in contact with the concrete. Further long-term experimental data from samples immersed in sulfate confirm findings reported in the CCAA publication TN68, of the very high resistance to sulfate conferred simply by low w/b. Natural environments having sulfate levels which are a threat to such concrete made with appropriate choice of binder are extremely rare. In acid sulfate soils, the sulfate component of acid produced by oxidation of pyrites is insignificant compared with the lowering of pH.

For exposure to groundwater containing chloride, moisture absorbed in the concrete will tend to this concentration by diffusion. While examples show steel free of corrosion under higher concentrations of chloride than would follow from direct contact with sea water, this level (about 2% in solution) can be chosen as a practical upper limit for design. However the steel will not necessarily remain passive if it is continuous into other environments able to disturb its potential relative to the surrounding concrete underground.

Specifications in the concrete pipe Standard AS/NZS 4058 are consistent with the information presented here, with the possible exception of exposure to high levels of sulfate, for which a requirement appears to be justified for the use of blended cement.

5. References

- 1. Bamforth, P., "Enhancing reinforced concrete durability", Technical Report No. 61, The Concrete Society, 2004.
- 2. Lea, F., "The chemistry of cement and concrete", Arnold, 1970.
- 3. Biczok, I., "Concrete corrosion and concrete protection", Akademiai Kiadó, Budapest, 1967.
- 4. Walpole, G. S., Journal of the Chemical Society **105**, 1914, p 2501.
- 5. Neville, A., "Properties of concrete", Pearson, 2011, Chapter 10.
- 6. Roark, R. J., "Formulas for stress and strain", 3rd edition, 1954.
- 7. fib Bulletin 34, "Model code for service life design", Lausanne, Switzerland, 2006.
- 8. "Durability of concrete construction", ACI Monograph 4, 1968.
- 9. "Durability and protection of concrete pipe in acid groundwater", Humes Concrete, 1999.
- 10. "Concrete in aggressive ground", Special Digest 1:2005, BRE Construction Division.
- 11. "Sulfate-resisting concrete", Technical Note 68, Cement, Concrete & Aggregates Australia, May 2011.
- 12. <u>Concrete Pipe in Acid Sulfate Soil Conditions</u>, Concrete Pipe Association of Australasia, 2012
- Glass, D. K. and Buenfeld, N. R., "Chloride threshold levels for corrosion induced deterioration of steel in concrete", RILEM International Workshop on Chloride Penetration into Concrete, St Remyles-Chevreuse, France, Eds Nilsson, L. O. and Ollivier, J.P., October 1995, Paper 3.
- 14. Harrison, N. L., "ISO 16204 and the correct solution to Fick", Concrete 2015, Concrete Institute of Australia, Melbourne, August 2015.
- 15. Glass,G. K., Reddy, B., Clark, L. A., "Making reinforced concrete immune from chloride corrosion", Construction Materials 160, November 2007 Issue CM4, pp 155-164.