AGGRESSIVE WATER ATTACK ON CARBONATED CEMENT MATERIALS

by

Grant Stewart Mackintosh
BSc (Civ. Eng.) Cape Town

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Water Research Group
Department of Civil Engineering
University of Cape Town

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Aggressive attack on samples was monitored by measuring changes in chemical characteristics of the water exposed to cement concrete samples, *inter alia* pH, calcium and alkalinity. Over the period of the investigation (100 days) the following observations were found to apply to both brown and white water :

(i) Generally uncarbonated OPC experiences significantly higher calcium mineral dissolution rates than both carbonated OPC and 30% fly ash OPC cement concretes.

(ii) Once steady dissolution rates were attained, measurements indicated that 30% fly ash OPC and carbonated OPC concrete undergo closely the same calcium mineral dissolution rates.

Before these findings are implemented, the following practical considerations need to be addressed :

(i) An ecomonic assessment of the benefits of using carbonated OPC, fly ash OPC and carbonated fly ash OPC as a means of resisting aggressive attack.

(ii) The investigation should be upgraded from laboratory scale to pilot scale.

(iii) The influence of accelerated carbonation on corrosion of steel reinforcing.

With regard to accelerated carbonation, i.e. (b) above, a literature survey revealed that accelerated carbonation is significantly influenced by curing regime. However, contradictory reports as to the influence of water curing period exist whilst no report on the influence of air curing period was to be found. As a result the second obective of this monograph was to enquire into the influence of curing regime on subsequent accelerated carbonation.

Two aspects of the influence of curing regime on accelerated carbonation were investigated. First, the influence of variable water curing period (with a fixed air curing period of 21 days), and second, the influence of variable air curing period (with a fixed water curing period of 14 days).

Measured carbonation depth with time in an atmosphere with a carbon dioxide partial pressure of 0,13 atmospheres was found to follow the widely accepted rate equation :

$$d_c = X_o + K\, t_c^{0,5}$$

where d_c = depth of carbonation (mm)
X_o = initial depth of carbonation (mm)
K = carbonation rate constant
t_c = exposure period (days).

With regard to the influence of curing regime, obsevations revealed :

(i) Carbonation rate decreased significantly with increased water curing period up to 7 days; further increase in water curing period has negligible influence.

(ii) The influence of air curing was similar to that of water curing but to a significantly reduced extent.

Recognising that the investigation into the influence of water curing on accelerated carbonation was carried out for a single fixed air curing period, and that the investigation into the influence of air curing period was carried out for a single fixed water curing period, it is recommended that the influence of water curing and air curing period on accelerated carbonation each be investigated over a range of air and water curing periods respectively.

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PREAMBLE

In most South African municipal water distribution systems approximately 90% of the pipes used will be composed of cement type materials and the remainder metal type. This arises for two reasons. First, cement-type pipes are cheaper than metal-type, and secondly, cement material does not undergo redox reactions in an aqueous environment so that corrosion and its pernicious results cannot occur. However, depending on the chemical characteristics of the water, dissolution of cement-type pipe material may occur with eventual pipe failure. This form of attack is termed aggression and the waters involved are termed aggressive.

The chemical characteristics of aggressive waters are usually reflected by low calcium and carbonate species concentrations and perhaps low pH. Waters with these characteristics can leach out calcium hydroxide and calcium carbonate species from the current matrix, thereby damaging the integrity of the material. Conversely, where the water being transported has high calcium and carbonate species concentrations, the dissolution of calcium hydroxide results in a rise in pH, supersaturation with respect to calcium carbonate, and precipitation of this mineral within the cement matrix. This process is termed aqueous phase carbonation. Once carbonation has occurred, and provided the chemical characteristics of the transported water are maintained with sufficient calcium and alkalinity, the pipe is protected from aggressive attack.

When a water brings about such carbonation of cement materials it is said to be stable with regard to aggression (this does not mean that it is necessarily stable with regard to corrosion of metals). The chemical quality criteria to attain such stability are sufficiently high dissolved calcium and carbonate species concentrations and that the water is just, or slightly, supersaturated with respect to calcium carbonate. Conversely a water is aggressive when it is undersaturated with respect to calcium carbonate.

When considering transportation of the brown waters of the South African southern and south-eastern seaboard regions, analysis shows that they and a pH less than about 6,0. As such, these waters are aggressive and aqueous phase carbonation will not occur. Progressive deterioration of the conduit can be expected. However, experience with transportation of these waters in concrete and asbestos cement pipes is variable. In most instances a very aggressive attack has been observed resulting in significant reduction in the design life of the pipe. Yet, in other instances, pipes have shown relatively little evidence of attack.

The greater resistance of some pipes to these so called brown waters has prompted investigation into possible reasons. Recognising that calcium hydroxide (lime) is significantly more soluble than calcium carbonate, it would appear that if a degree of carbonation was able to occur prior to commissioning of the pipe, this could in some measure reduce the rate of aggressive attack on the concrete. Such carbonation could occur from the gaseous phase via atmospheric carbon dioxide diffusing into the concrete and reacting with calcium hydroxide to form calcium carbonate, i.e. <u>gaseous phase carbonation</u>. If, in fact, this layer of calcium carbonate is able to provide significantly better protection than uncarbonated cement to brown water attack, then the ability to create such a layer through the use of accelerated gaseous phase carbonation techniques could have important implications when considering the transportation of natural waters.

In this report an experimental study was undertaken to investigate the validity of the above hypothesis, i.e. the ability of a calcium carbonate skin to provide protection to concrete conduits and cement type pipes from brown water attack. As such the study consists of the following two main objectives, to investigate :

A. the effectiveness of a carbonated layer to protect concrete from aggressive white and brown water attack

B. accelerated gaseous phase carbonation.

These two objectives are achieved by splitting this report into the above two sections, namely A and B.

SECTION A

CHAPTER 1

DISSOLUTION OF CEMENT CONCRETE IN AGGRESSIVE ENVIRONMENTS

1.1 INTRODUCTION

Concrete and cement lined water structures containing or transporting water may be vulnerable to attack as a result of the chemical characteristics of the water (Eglinton, 1975; Fattuhi and Hughes, 1983; Gutt and Harrison, 1977; Halstead, 1954). When attack occurs the water is termed aggressive and the phenomenon is termed aggression. Two well recognised forms of aggressive attack have been identified (Loewenthal *et al*, 1986) :

1. Dissolution of free lime ($Ca(OH)_2$) and/or carbonated lime ($CaCO_3$) out of the cement matrix resulting in deterioration of the concrete's properties.

2. Physical disruption of the matrix due to transformation of certain matrix minerals to a product with a higher specific volume than the original mineral. (Transformation of calcium aluminates in the cement matrix to calcium sulphoaluminate due to high sulphate concentration in the transported water body (> 350 mg/ℓ SO_4^{2-}) is the dominant cause of this phenomena).

In this report aggression due to lime and calcium carbonate dissolution (i.e. (1) above) is considered. This form of aggression arises as follows: Hardened cement in cement concrete consists of a matrix mainly of free lime, magnesium oxide, hydrated di- and tricalcium silicates, tricalcium aluminates and tetra-calcium alumino ferrites (Fulton, 1977). If the chemical characteristics of the water are such that it causes dissolution of free lime ($Ca(OH)_2$) and/or carbonated lime ($CaCO_3$) at the outer surfaces of the cement mass, these minerals will be progressively removed resulting in weakening of the cement matrix (Harrison, 1987; Kunzler and Schwenk, 1986; Millette *et al*, 1980; Muller, 1978). This type of attack has been noted to occur with :

(a) so called "white" and "brown" waters with low calcium, low alkalinity (each less than 30 mg/ℓ as $CaCO_3$), low pH and undersaturated with respect to $CaCO_3$[1] (termed alkalinity/calcium deficient waters).

(b) waters with relatively high calcium, alkalinity and pH but undersaturated with respect to $CaCO_3$.

Low alkalinity, calcium waters (both white and brown) occur along the southern and south eastern region of South Africa. Rivers and streams draining these regions are underlain principally by quartzites, sandstones and shales of the Table Mountain and Bokkeveld series. Weathering of these series gives rise to the formation of well leached, acid soils such that the surface waters characteristically have low total alkalinity (0-20 mg/ℓ as $CaCO_3$), low calcium (0-20 mg/ℓ as $CaCO_3$) and low pH (4,0-6,0). These waters tend to contain significant concentrations of dissolved organic (humic) substances derived from the decomposition of vegetation under the prevailing acid conditions (Gardiner, 1989). The humic substances comprise mainly humic and fulvic acids with concentrations and specific properties which vary seasonly and between catchment areas. The waters range in colour from crystal clear to dark brown, hence the colloquial references to "white" and "brown" waters.

The higher calcium and alkalinity waters with aggressive characteristics (i.e. (b) above) usually arise in underground waters; the relatively low pH ($6 \leq pH \leq 7$) arises from dissolution of carbon dioxide (CO_2) in an environment with high partial pressure of CO_2 relative to that of the air. The general observation for the action of these acidic underground waters is that they are aggressive to cement type materials unless aerated to a degree where aqueous-gaseous equilibrium is attained. However, observations of the influence of the low calcium/alkalinity waters on cement type materials are variable; reports indicate that both significant and negligible rates of attack have been recorded. This variability may arise from either, or both, of two sources :

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[1]

1. Variability of the $CaCO_3$ dissolving potential of the water. Normally the Langelier Saturation Index (L.S.I.) is used to indicate whether water is $CaCO_3$ dissolving or scaling (see later), however, the value of this index only indicates super or undersaturation giving no indication of the magnitude. Clearly it is the magnitude of the $CaCO_3$ dissolving potential which will dictate the degree of attack by the water of the cement material.

2. Variability in the chemical nature of the cement material surface. Over and above differences in the physical characteristics between various cement types, the degree of carbonation of the free lime is likely to be variable depending on the history of the conduit or cement structure. In this regard, for a particular water quality, the rate of dissolution of free lime is likely to differ from that of the carbonated lime. Furthermore, the occurrences of dissolved humic substances and their effect on the aggressiveness of the water is a further unknown entity (Robertson and Rashid, 1976).

The objective of Section A of this investigation is to enquire into the ability of various cement types to withstand attack from aggressive waters (both white and brown). The cement types investigated are :

(a) Ordinary Portland Cement,

(b) Carbonated Ordinary Portland Cement

(c) 30% Fly Ash mix with Ordinary Portland Cement.

Clearly such an investigation requires that the degree (and rate) of attack be monitored. This can be achieved by either or both :

1. measuring physical changes to the concrete (e.g. weight loss and strength changes), and/or

2. measuring changes in the chemical characteristics of the water arising from dissolution of cement material due to aggression.

Whereas the former approach requires inordinately large lengths of time (years) to obtain meaningful results, the latter approach can be used for both short (months) and long term investigations. Due to time limitations the latter approach was adopted for this investigation. Clearly its application requires an in-depth understanding of the aqueous and aqueous-solid phase chemistry for waters with and without dissolved humic substances.

This section, therefore, includes the following chapters :

Chapter 2.	Chemistry of the carbonate system in the aqueous phase.
Chapter 3.	Chemistry of the calcium/carbonate system considering aqueous, solid and gas phases.
Chapter 4.	A literature review on the nature and influence of dissolved humic substances in water.
Chapter 5.	Experimental investigation into the dissolution of cement concrete materials by brown and white aggressive water.
Chapter 6.	General conclusions.

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SECTION A

CHAPTER 2

CHEMISTRY OF THE CARBONATE SYSTEM IN THE AQUEOUS PHASE

2.1 INTRODUCTION

Solid $CaCO_3$ or $Ca(OH)_2$ will dissolve into water only if the solution is undersaturated with respect to these minerals. When this occurs the dissolution rate can be monitored by considering the stoichiometric changes in water characteristics as the mineral dissolves. These can be determined from chemical equilibrium considering the aqueous phase only. However, the maximum mass concentration of mineral which can ultimately dissolve into the water is reached when the water is just saturated with respect to the solid mineral; for this condition carbonate species concentration will be governed by equilibrium between species in the aqueous and solid phases, i.e. two phase equilibrium. Thus for the purposes of monitoring the changes in chemical state of a water bringing about mineral dissolution, one is concerned only with single phase equilibrium. Yet, in order to assess the relative aggressiveness of the water to cement type materials it is necessary to consider the saturation state, i.e. two phase (aqueous-solid) equilibrium.

This chapter covers single aqueous phase equilibrium; under which the fundamentally important mass parameters Alkalinity and Acidity are introduced and the interdependence between these mass parameters is dealt with.

2.2 CARBONATE SPECIES EQUILIBRIA

In terrestrial waters not containing humic substances the carbonate system is the dominating one to such a degree that other weak acid/base systems usually are neglected. The carbonate system in aqueous solution is comprised of the species molecularly dissolved carbon dioxide, CO_{2aq} , carbonic acid, H_2CO_3 , and the ionic species bicarbonate, HCO_3^- , and carbonate, CO_3^{2-} . These dissolved species exist in equilibrium with each other and with the water species, OH^- and H^+ .

The relative concentrations of the dissolved species are governed by chemical equilibrium which leads to the following dissociation equations for the carbonate system in water.

For the water species :

$$(H^+)\ [OH^-] \ = \ K_w/F_m \ = \ K'_w \tag{2.1}$$

For the carbonate species :

$$(H^+)\ [HCO_3^-]\ /\ [H_2CO_3^*] \ = \ K_1/F_m \ = \ K'_1 \tag{2.2}$$

$$(H^+)\ [CO_3^{2-}]\ /\ [HCO_3^-] \ = \ K_2\ F_m\ /\ F_d \ = \ K'_2 \tag{2.3}$$

where $[H_2CO_3^*]$ = the sum of molecularly dissolved carbon dioxide $[CO_2]_{aq}$, and carbonic acid, $[H_2CO_3]$, mol/ℓ

K_1, K_2, K'_1, K'_2 = thermodynamic and apparent dissociation equilibrium constants respectively for the carbonate system

K_w, K'_w = thermodynamic and apparent ionic product constants respectively for water system

F_m, F_d = monovalent and divalent activity coefficients (see Appendix A)

[ ], ( ) = molar mass and active mass (activity) respectively.

The equilibrium constants K_w , K_1 and K_2 in Equations (2.1) to (2.3) vary with temperature as follows :

(a) For pK_w from Harned and Hamer (1933)

$$pK_w = 4787{,}3/(T) + 7{,}1321 \log (T) + 0{,}01037\ (T) - 22{,}801$$
$$= 14{,}165 \text{ at } 20°C$$

(b) For pK_1 from Harned and Davies (1943)

$$pK_1 = 17052/(T) + 215{,}21 \log (T) - 0{,}12675 (T) - 545{,}56$$

$$= 6{,}394 \quad \text{at} \quad 20°C$$

(c) For pK_2 from Harned and Scholes (1943)

$$pK_2 = 2902{,}39/(T) + 0{,}02379 (T) - 6{,}498$$

$$= 10{,}377 \quad \text{at} \quad 20°C$$

where : $pX = - \log X$

T = temperature in Kelvin.

In the dissociation Equations (2.1) to (2.3) above the hydrogen ion concentration is expressed in the active form, (H^+). This arises because this parameter is measured in this form via pH using potentiometric methods where

$$pH = - \log (H^+) \qquad (2.4)$$

and thus the numerical value of (H^+) is as follows :

$$(H^+) = 10^{-pH} .$$

The three equilibrium equations above (i.e. Equations 2.1 to 2.3) incorporate five unknowns, i.e. (H^+), $[OH^-]$, $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$, so that to determine values for all these parameters (i.e. to characterise the system) two independent parameters must be measured. From Equation (2.4) it can be seen that the measurement of pH satisfies one of these requirements; direct measurement of any one of the other parameters is not possible. However, there exist further parameters for the system which "are linked" to the individual species concentrations and which can be measured. These include various capacity parameters such as total carbonate species concentrations and various forms of alkalinity and acidity.

2.3 MASS PARAMETERS - TOTAL CARBONATE SPECIES, ALKALINITY AND ACIDITY

2.3.1 Total carbonate species

The total carbonate species concentration, C_T , is defined as :

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{2.5}$$

Clearly if C_T and pH are measured the system can be characterised. The distribution of carbonate and water species with pH for a fixed C_T is shown graphically in a log species-pH diagram in Figure 2.1. However, measurement of C_T requires expensive laboratory equipment (i.e. an inorganic carbon analyser) so that this parameter is seldom used explicitly in characterisation.

Invariably as an alternative to C_T measurement one (or more) of the various forms of alkalinity or acidity are measured and used in characterisation. Definitions and equations for the various forms of alkalinity and acidity are not as obvious as that for total carbonate species and are, therefore, introduced only after a conceptual explanation in the following section. (Suffice to note, however, that these parameters are relatively easily measured in practice and thus are commonly used with pH for characterisation purposes).

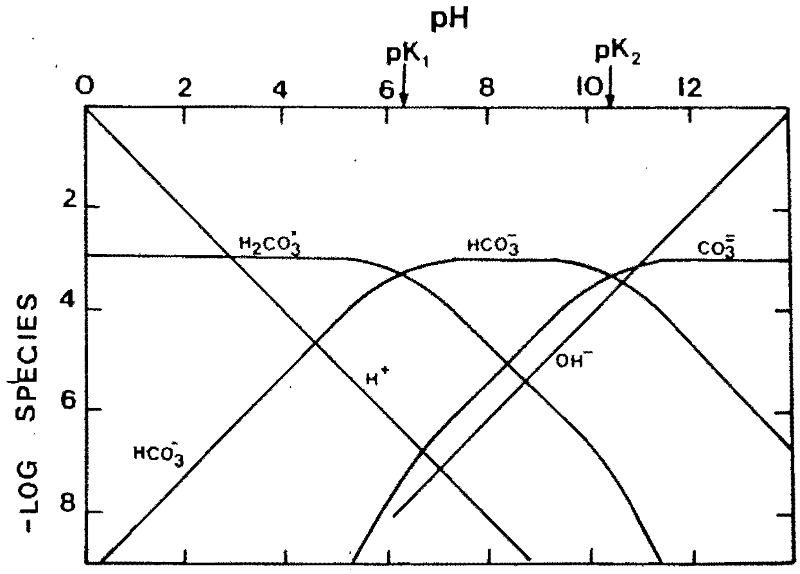

Figure 2.1 : Log species-pH plot for the carbonate system in water

2.3.2 Alkalinity and acidity

Alkalinity (acidity) is defined as the proton accepting (donating) capacity of a solution relative to some reference state. The reference state is an equivalent solution for water containing only one weak acid system, the equivalent solutions formed by the addition of either a weak acid or its salt to pure water and the pH established is termed the equivalence point. Likewise, addition of HCO_3^- or CO_3^{2-} species to pure water results in the formation of an equivalent HCO_3^- or CO_3^{2-} solution with a pH of the HCO_3^- or CO_3^{2-} equivalence point respectively.

The term alkalinity thus implies the presence of a net strong base (alkali) which has been added to an equivalent solution of either $H_2CO_3^*$, HCO_3^- or CO_3^{2-} to change the pH from that of the equivalence point to the observed pH. Standard strong base together with an equivalent $H_2CO_3^*$ solution is termed $H_2CO_3^*$ alkalinity, Alkalinity or total alkalinity; standard strong base with an equivalent HCO_3^- solution is termed HCO_3^- alkalinity or phenolthalein alkalinity and standard strong base with an equivalent CO_3^{2-} solution is termed CO_3^{2-} alkalinity or caustic alkalinity.

Equations for the various forms of alkalinity in terms of weak acid species are developed from proton balances (see Loewenthal *et al*, 1989) and are as follows :

(a) $H_2CO_3^*$ alkalinity (i.e. Alkalinity or total alkalinity) :

An equivalent $H_2CO_3^*$ solution plus a net strong base,

$$H_2CO_3^* \text{ alkalinity} = 2\,[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \qquad (2.6)$$

(b) HCO_3^- alkalinity (i.e. phenolpthalein alkalinity) :

An equivalent HCO_3^- solution plus a net strong base,

$$HCO_3^- \text{ alkalinity} = [CO_3^{2-}] + [OH^-] - [H_2CO_3^*] - [H^+] \qquad (2.7)$$

(c) CO_3^{2-} alkalinity (i.e. caustic alkalinity) :

An equivalent CO_3^{2-} solution plus a net strong base

$$CO_3^{2-} \text{ alkalinity} = [OH^-] - 2\,[H_2CO_3^*] - [HCO_3^-] - [H^+] \tag{2.8}$$

Similarly, the term acidity implies the presence of a net strong acid (acidity) which has been added to an equivalent solution of either $H_2CO_3^*$, HCO_3^- or CO_3^{2-} to change the pH from that of the equivalence point to the observed pH. Following along similar lines to the alkalinity equations, equations in terms of weak acid species concentrations for the forms of acidity are developed from proton balances (see Loewenthal *et al*, 1989) and are as follows :

(a) CO_3^{2-} acidity (i.e. Acidity or total acidity) :

An equivalent CO_3^{2-} solution plus a net strong acid,

$$CO_3^{2-} \text{ acidity} = [HCO_3^-] + 2\,[H_2CO_3^*] + [H^+] - [OH^-] \tag{2.9}$$

(b) HCO_3^- (i.e. CO_3^{2-} acidity) :

An equivalent HCO_3^- solution plus a net strong acid,

$$HCO_3^- \text{ acidity} = [H_2CO_3^*] + [H^+] - [CO_3^{2-}] - [OH] \tag{2.10}$$

(c) $H_2CO_3^*$ (i.e. mineral acidity) :

an equivalent $H_2CO_3^*$ solution plus a net strong acid,

$$H_2CO_3^* \text{ acidity} = [H^+] - 2\,[CO_3^{2-}] - [HCO_3^-] - [OH^-] \tag{2.11}$$

In order to make use of various forms of alkalinity and acidity (i.e. Equations 2.6 to 2.11) to characterise water, accurate measurement of one or more of these mass parameters is necessary and is discussed in the following section.

2.3.3 Measurement of alkalinity and acidity

For the carbonate system three equivalent solutions can be formed by adding either CO_2 , HCO_3^- or CO_3^{2-} to water. If a strong base (acid) is added to any of the respective equivalent solutions, the pH changes away from that of the equivalence point. The mass of base (acid) added is called the alkalinity (acidity) relative to the equivalent solution. This alkalinity (acidity) is determined experimentally by titrating back to the equivalent solution with a standard strong acid (base). Measurement of $H_2CO_3^*$, HCO_3 and CO_3^{2-} alkalinity thus involves incremental addition of a standard strong acid to a known volume of sample till the respective equivalence points for the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalent solutions. Similarly, we obtain CO_3^{2-} , HCO_3^- and $H_2CO_3^*$ acidities by titrating with a strong base till the respective equivalence points for the CO_3^{2-} , HCO_3^- and $H_2CO_3^*$ equivalent solutions are reached.

In Figure 2.2 is shown a plot of the log of carbonate species concentrations versus pH for the carbonate system. Also shown are the equivalence points to which titration is carried out in measuring the various forms of alkalinity and acidity. Prior to the time when pH meters came into general use the $H_2CO_3^*$ and HCO_3^- equivalence points were determined approximately by using the colour pH indicators, methyl orange and phenolpthalein respectively. However, with the availability and general use of pH meters, the end point can be readily and conveniently determined with greater accuracy.

Only two independent parameters are necessary for characterising the carbonate system in the aqueous phase. Usually pH forms one of these because it can be quickly and accurately measured; the second parameter to be measured will be one of the various forms of alkalinity and acidity. It is pertinent, therefore, to critically assess which of these is of the most practical value.

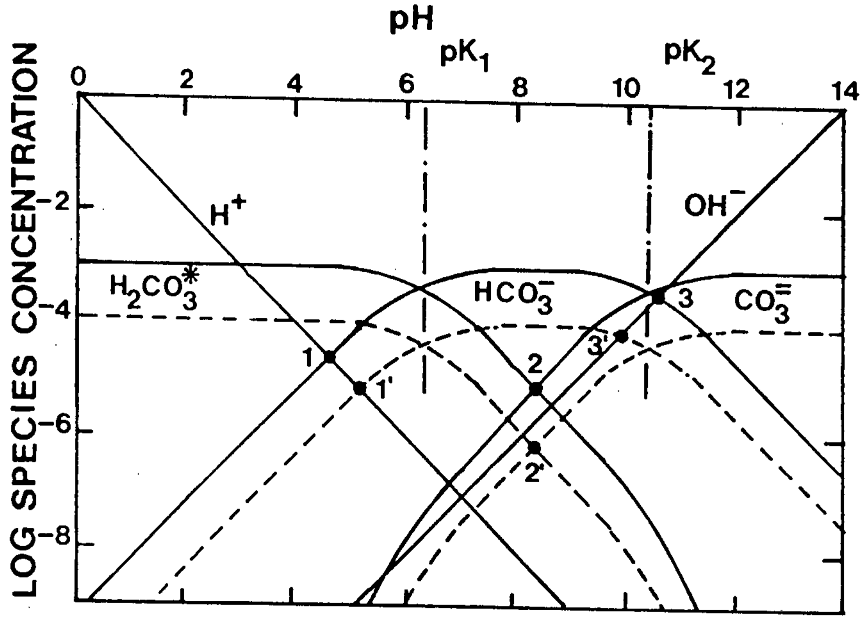

Figure 2.2 : Log species-pH diagrams for two waters with $C_T = 10^{-3}$ and 10^{-4} mol/ℓ. $H_2CO_3^*$ equivalence point occurs at pH Points 1 and 1' and varies with C_T. HCO_3^- equivalence point occurs at pH of Points 2 and 2' and is independent of C_T .

(a) Alkalinity or acidity to the $H_2CO_3^*$ equivalence point

Titration to the $H_2CO_3^*$ equivalence point has the advantage that $H_2CO_3^*$ alkalinity is not affected by loss or gain of CO_2 so that it can be measured even if there is a loss of CO_2 after sampling or during measurement. However, the experimental measurement does present a problem in that the equivalence point depends strongly on the total carbonate species concentration, C_T , which is unknown and changes with CO_2 loss (or gain). Despite this apparent difficulty, procedures have been developed whereby one can select the end point pH with sufficient accuracy provided the $H_2CO_3^*$ alkalinity is greater than about 30 mg/ℓ as $CaCO_3$ (Standard Methods, 1985). Fortunately, the $H_2CO_3^*$ equivalence point lies in a pH region of low buffering capacity so that slight errors in the equivalence point estimation do not give rise to significant errors in the $H_2CO_3^*$ alkalinity, except when the alkalinity is low where large relative errors will arise.

Fortunately, however, where highly accurate measurement of $H_2CO_3^*$ alkalinity is required, this can be achieved without using an endpoint titration by employing a potentiometric titration method developed by Gran (1952). Gran titrations and procedures to determine appropriate alkalinities and acidities are set out in Appendix B.

(b) Alkalinity or acidity to the HCO_3^- equivalence point

Measurement of alkalinity or acidity to the HCO_3^- equivalence point has the following advantages :

(i) The equivalence point lies in a region of very low buffer capacity so that titration errors are usually negligible. (A Gran titration, as set out in Appendix B, can be used for high accuracy).

(ii) The endpoint is virtually independent of C_T .

However, measurement to this equivalence point has the following disadvantages :

(i) For waters with pH close to the HCO_3^- equivalence point, it is not possible to characterise the carbonate weak acid system accurately from measurement of pH and HCO_3^- alkalinity/acidity. This is because a small error in measurement of either these two parameters results in relatively large errors in the calculated values for C_T and other forms of alkalinity and acidity.

(ii) Loss or gain of CO_2 from the air by the sample causes an error in the measurement equal to the molar mass concentration of CO_2 exchanged (see later).

(c) Alkalinity or acidity to the CO_3^{2-} equivalence point

This measurement by titration is not practical for the following reasons :

(i) The pH of the endpoint changes with C_T .

(ii) The endpoint cannot be identified in the pH titration curve with any accuracy.

(iii) The titration is in a high pH region; at high pH the water tends to absorb CO_2 from the air causing an error in measurement equal to twice the molar mass concentration of CO_2 absorbed (see later).

(iv) The CO_3^{2-} equivalence point lies in a region of high buffering capacity so that small errors in the titrated endpoint result in large titration errors.

2.4 INTERDEPENDENCE BETWEEN MASS PARAMETERS ALKALINITY, ACIDITY AND TOTAL SPECIES CONCENTRATION

The mass parameters alkalinity, acidity and total species concentration are parameters which can be used to determine (or characterise) the state of a water. Consequently, in terms of what was stated previously, one would expect that if values for any two of these parameters are known the remaining parameters can be determined. That is, one expects some form of interdependency between these parameters. Two forms of interdependence exist :

(a) between alkalinities and acidities with the same reference equivalent solution, and

(b) between alkalinities and acidities relative to different equivalent solutions.

(a) For the alkalinity and acidity associated with the same equivalence solution, the alkalinity value is simply the negative of the acidity value, e.g. from Equations (2.6) and (2.11)

$$H_2CO_3^* \text{ alkalinity} = -H_2CO_3^* \text{ acidity} \qquad (2.12)$$

(b) The sum of alkalinity with respect to a selected equivalent solution and acidity with respect to the next lower protonated equivalent solution equals total carbonate species concentration, i.e.

$$H_2CO_3^* \text{ alkalinity} + HCO_3^- \text{ acidity} = C_T \qquad (2.13)$$

$$HCO_3^- \text{ alkalinity} + CO_3^{2-} \text{ acidity} = C_T \qquad (2.14)$$

More broadly, if the reference species for the equivalent solution relative to which alkalinity and acidity are defined are "n" protons apart the sum is 'n' times C_T, e.g. :

$$H_2CO_3^* \text{ alkalinity} + HCO_3^- \text{ acidity} = C_T \quad (n = 1) \qquad (2.15)$$

$$H_2CO_3^* \text{ alkalinity} + CO_3^{2-} \text{ acidity} = 2C_T \quad (n = 2) \qquad (2.16)$$

These relationships can be represented graphically as shown in Figure 2.3. This plot shows that if values are known for two independent mass parameters then values for the remaining mass parameters can be determined directly.

For example, if say, $H_2CO_3^*$ alkalinity = 2 mmol/ℓ and HCO_3^- acidity = 1 mmol/ℓ, then from above section

$$\begin{aligned} C_T &= H_2CO_3^* \text{ alkalinity} + HCO_3^- \text{ acidity} \\ &= 3 \text{ mmol/ℓ} \end{aligned}$$

$$\begin{aligned} HCO_3^- \text{ alkalinity} &= -HCO_3 \text{ acidity} \\ &= -1 \text{ mmol/ℓ} \end{aligned}$$

$$\begin{aligned} CO_3^{2-} \text{ alkalinity} &= -CO_3^{2-} \text{ acidity} \\ &= -4 \text{ mmol/ℓ} \end{aligned}$$

$$H_2CO_3^* \text{ acidity} = -H_2CO_3 \text{ alkalinity}$$
$$= -2 \text{ mmol}/\ell$$

$$CO_3^{2-} \text{ acidity} = C_T - HCO_3^- \text{ alkalinity}$$
$$= 4 \text{ mmol}/\ell$$

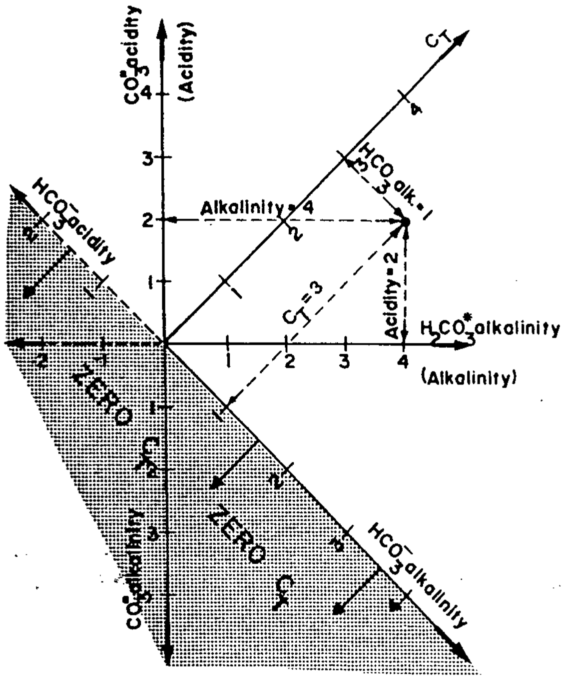

Figure 2.3 : Interdependence between mass parameters for the carbonate system.

2.5 INTERDEPENDENCE BETWEEN pH AND MASS PARAMETERS

As set out above, measurement of two independent parameters for the carbonate system automatically yields values for the remaining parameters. Those most easily and accurately measured are pH and $H_2CO_3^*$ alkalinity. If CO_3^{2-} acidity is now to be calculated, then a relationship linking this parameter to the two measured parameters (i.e. pH and $H_2CO_3^*$ alkalinity) can be formulated using the equilibrium

Equations (2.1) to (2.3) and those for alkalinity and acidity, Equations (2.6) and (2.9), giving[1]

$$\text{Acidity} = [\text{Alk} - 10^{(pH - pK'_w)} + 10^{-pH}] * \left(\frac{1+2.10^{(pK'_1-pH)}}{1+2.10^{(pH-pK'_2)}}\right) - 10^{(pH-pK'_w)} + 10^{-pH} \qquad (2.17)$$

Examination of Equation (2.17) shows that for a chosen pH value there exists a linear relationship between Alkalinity and Acidity. In Figure 2.4 a plot of Alkalinity versus Acidity for a range of pH values is shown.

Figure 2.4, known as a Deffeyes type conditioning diagram (Loewenthal and Marais, 1976), shows that the measurement of any two independent parameters completely defines the values for the remaining ones. For example, if pH and Alkalinity are known the value for Acidity is simply read off the appropriate ordinate. Alternatively, if Acidity and Alkalinity are known pH can be interpolated.

An important aspect of the Alkalinity-Acidity-pH diagram is that it can be used to predict the change in state of a water due to chemical dosing and, as such, constitutes a single phase conditioning diagram. Fundamental to the use of this diagram as a conditioning diagram are the simple stoichiometric changes in the mass parameters with dosing.

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[1] The parameters $H_2CO_3^*$ alkalinity and CO_3^{2-} acidity are often termed total alkalinity and total acidity or simply Alkalinity and Acidity respectively.

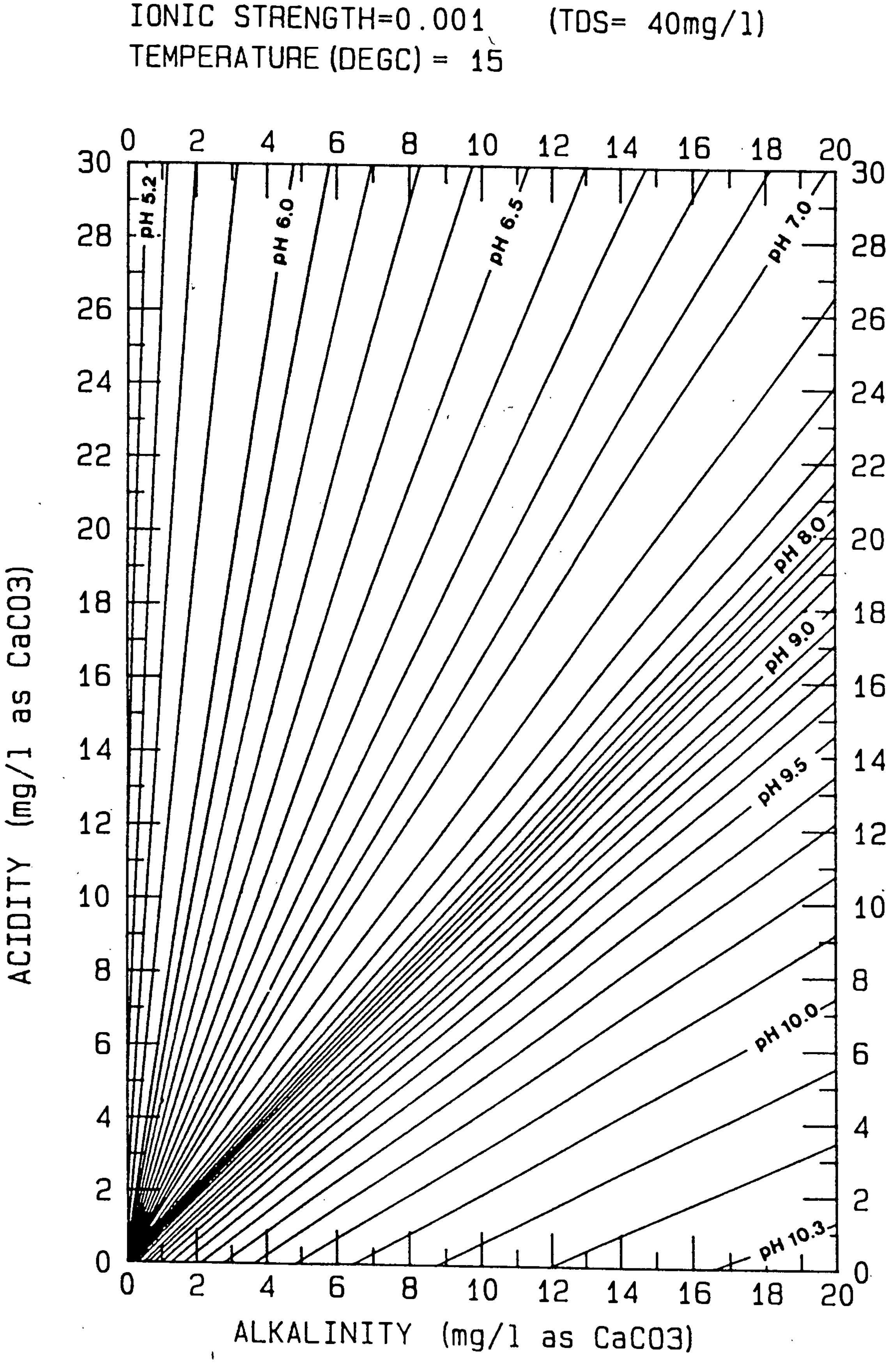

Figure 2.4 : Plot of pH lines with Alkalinity and Acidity as axes parameters constitutes a Deffeyes type diagram.

2.6 CHANGES IN MASS PARAMETERS WITH CHEMICAL DOSING

When a solution is dosed, whereas pH and individual species concentrations change in a complex fashion, the mass parameters (C_T, Alkalinity and Acidity) change in a simple stoichiometric manner as follows :

$$\Delta\ H_2CO_3^*\ \text{alkalinity} = 2\ [CO_3^{2-}]\ (\text{added}) + [HCO_3^-]\ (\text{added}) + [OH^-]\ (\text{added}) - [H^+]\ (\text{added}) \qquad (2.18)$$

$$\Delta\ CO_3^{2-}\ \text{acidity} = 2\ [H_2CO_3^*]\ (\text{added}) + [HCO_3^-]\ (\text{added}) + [H^+]\ (\text{added}) - [OH^-]\ (\text{added}) \qquad (2.19)$$

$$\Delta\ C_T = [H_2CO_3^*]\ (\text{added}) + [HCO_3^-]\ (\text{added}) + [CO_3^{2-}]\ (\text{added}) \qquad (2.20)$$

where Δ = increase.

Whereas the change in C_T with dosing (Equation 2.20) is self-evident, those for $H_2CO_3^*$ alkalinity and CO_3^{2-} acidity (Equations 2.18 and 2.19) are not. (The reader is referred to the work of Loewenthal *et al* (1986) for their derivations).

The interdependencies between the mass parameters are still valid in terms of the changes in each of the parameters with dosing. For example, considering changes in $H_2CO_3^*$ alkalinity, CO_3^{2-} acidity and C_T .

i.e. $$\Delta\ H_2CO_3^*\ \text{alkalinity} + \Delta\ CO_3^{2-}\ \text{acidity} = [CO_3^{2-}]\ (\text{added}) + 2\ [HCO_3^-]\ (\text{added}) + [H_2CO_3^*]\ (\text{added}) = 2\ C_T\ (\text{change})$$

where Δ = increase.

Thus, if x, y and z mmol/ℓ of $H_2CO_3^*$, HCO_3^- and CO_3^{2-} respectively and A and B mmol/ℓ of strong acid and strong base respectively, are added to water the Alkalinity, Acidity and C_T changes are, from Equations (2.18) to (2.20) :

$$\Delta\ H_2CO_3^*\ \text{alkalinity} = 2z + y + B - A$$

$$\Delta\ CO_3^{2-}\ \text{acidity} = 2x + y + A - B$$

$$\Delta\ C_T = x + y + z$$

where Δ = increase.

Equations (2.18) and (2.19) show that changes in mass parameters with chemical dosing can be determined very simply. These simple stoichiometric changes in capacity parameters with dosing, coupled with the single aqueous phase conditioning diagram formulated earlier, form the basis for monitoring concrete/cement dissolution experiments reported in Chapter 5. For example, if an aggressive water is in contact with cement by monitoring the changes in Alkalinity, HCO_3^- alkalinity is possible to determine the amount of $Ca(OH)_2$ that has gone into the aqueous phase as follows :

$H_2CO_3^*$ alkalinity$_i$ = 0,0 $\quad$ $H_2CO_3^*$ alkalinity$_f$ = 81,1 mmol/ℓ

HCO_3^- alkalinity$_i$ = 0,0 $\quad$ HCO_3^- alkalinity$_f$ = 81,1 mmol/ℓ

where i = initial
f = final.

Then from Equation (2.18) the amount of free lime that has gone into solution is :

$$(H_2CO_3^*\ \text{alk}_f - H_2CO_3^*\ \text{alk}_i)/2 = 81{,}1/2 = 40{,}55\ \text{mmol}/\ell.$$

2.7 THE $CaCO_3$ CONCENTRATION SCALE

Three concentration scales are commonly used in aquatic chemistry; these are the molar, equivalent and "mg/ℓ as $CaCO_3$" scales. The molar scale is recommended by the IUPAC (International Union of Pure and Applied Chemists). However, water chemists and concrete technologists, when addressing the calcium carbonate system in aqueous solutions, usually use the "mg/ℓ as $CaCO_3$" scale. This arises as a result of historical precedence rather than practical convenience. In this monograph the two scales will be used interchangeably; but clarity will always be made as to which scale is being used. For the sake of convenience conversion between the two scales is set out below :

(a) Conversion to the $CaCO_3$ scale : The concentration of substance 'A' in "mg/ℓ as $CaCO_3$" is determined as follows :

(i) If A is expressed in g/ℓ (i.e. mass scale)

$$\text{mg}/\ell \text{ of A as } CaCO_3 = \frac{(\text{g of A}/\ell)}{MW_A} \cdot n_A . EW_{CaCO_3} \cdot 10^3 \qquad (2.21)$$

where EW_{CaCO_3} = equivalent weight of $CaCO_3$ = 50 g

n_A = charge on species A (for ions) and equal to the number of hydrogen ions or hydroxyl ions that react with species A (for neutral species), i.e. n = 2 for $Ca(OH)_2$, $H_2CO_3^*$, Na_2CO_3 , H_2SO_4 and $CaCO_3$; n = 1 for NaOH, HCL and $NaHCO_3$.

MW_A = molecular weight of substance A in grams

(ii) if A is expressed in the molar form,

$$\text{mg}/\ell \text{ of A as } CaCO_3 = (\text{moles of A}/\ell).n_A.EW_{CaCO_3}.10^3 \qquad (2.22)$$

(b) Mass balance equations on the $CaCO_3$ scale :

Transformation of the the various mass balance expressions from the molar to the $CaCO_3$ scale is achieved by substituting the molar form with the $CaCO_3$ form as described by Equation (2.22) giving the following :

$$H_2CO_3^* \text{ alkalinity} = CO_3^{2-} + HCO_3^- + OH^- - H^+ \quad (2.23)$$

$$HCO_3^- \text{ alkalinity} = CO_3^{2-}/2 + OH^- - H_2CO_3^*/2 - H^+ \quad (2.24)$$

$$CO_3^{2-} \text{ alkalinity} = OH^- - H^+ - HCO_3^- - H_2CO_3^* \quad (2.25)$$

$$CO_3^{2-} \text{ acidity} = H_2CO_3^* + HCO_3^- + H^+ - OH^- \quad (2.26)$$

$$HCO_3^- \text{ acidity} = H_2CO_3^*/2 + H^+ - CO_3^{2-}/2 - OH^- \quad (2.27)$$

$$H_2CO_3^* \text{ acidity} = H^+ - CO_3^{2-} - HCO_3^- - OH^- \quad (2.28)$$

$$C_T = H_2CO_3^*/2 + HCO_3^- - CO_3^{2-}/2 \quad (2.29)$$

(Where the use of no brackets indicates that species concentrations are expressed in mg/ℓ as $CaCO_3$).

It should be noted that the expressions for the interdependence between the various mass parameters, Equations (2.12) to (2.16), are independent of the concentration scale and are still valid for species concentrations on the $CaCO_3$ scale. However, the changes in mass parameters with chemical dosing (section 2.6) will alter when the $CaCO_3$ concentration scale is adapted. From Equations (2.23) to (2.29) it can be seen that these changes are as follows :

$$\Delta\ H_2CO_3^* \text{ alkalinity} = CO_3^{2-} \text{ (added)} + HCO_3^- \text{ (added)} + OH^- \text{ (added)} - H^+ \text{ (added)} \quad (2.30)$$

$$\Delta\ CO_3^{2-} \text{ acidity} = H_2CO_3^* \text{ (added)} + HCO_3^- \text{ (added)} + H^+ \text{ (added)} - OH^- \text{ (added)} \quad (2.31)$$

$$\Delta\ C_T = H_2CO_3^* \text{ (added)}/2 + HCO_3^- \text{ (added)} + CO_3^{2-} \text{ (added)}/2 \qquad (2.32)$$

where Δ = increase.

Thus, if x, y and z mg/ℓ as $CaCO_3$ of $H_2CO_3^*$, HCO_3^- and CO_3^{2-} respectively, and A and B mg/ℓ as $CaCO_3$ of strong acid and strong base respectively, are added to water the Alkalinity, Acidity and C_T changes are, from Equations (2.30) to (2.32) :

$$\Delta\ H_2CO_3^* \text{ alkalinity} = z + y + B - A$$

$$\Delta\ CO_3^{2-} \text{ acidity} = x + y + A - B$$

$$\Delta\ C_T = x/2 + y + z/2$$

where Δ = increase.

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SECTION A

CHAPTER 3

CHEMISTRY OF THE CARBONATE SYSTEM IN THE AQUEOUS, GASEOUS AND SOLID PHASES

3.1 INTRODUCTION

The discussion in Chapter 2 summarises the chemical aspects of the carbonate system in the aqueous phase. Changes in the aqueous phase chemical characteristics of a water *inter alia* either exchanging carbon dioxide with the gaseous phase or dissolving/precipitating minerals, is assessed using single aqueous phase equilibrium considerations as described. However, no consideration was given to the "driving forces" with respect to interphase equilibrium, i.e. water brought into contact with a gaseous phase (say carbon dioxide in the air) or a solid phase (say calcite).

For carbon dioxide exchange with the gas phase the driving force is induced by a state of disequilibrium between molecularly dissolved carbon dioxide in the aqueous phase and carbon dioxide in the gaseous phase. For calcium carbonate precipitation/dissolution, the driving force is induced by disequilibrium between calcium and carbonate species in the aqueous phase and, say, calcite ($CaCO_3$), in the solid phase. Compared with rates to equilibrium between species in the aqueous phase, rates for interphase equilibrium are inevitably very much slower and will depend on such factors as degree of disequilibrium, mixing, etc.

In this investigation, equilibrium between species in the aqueous and solid phases is of primary interest. However, as will be shown shortly, equilibrium between aqueous and solid phase species of a mineral is influenced by aqueous-gaseous interaction. Before assessing quantitatively the changes which occur as interphase equilibrium is attained, it is necessary first to discuss briefly the state of equilibrium occurring between both the aqueous and gaseous phases and/or the solid phase. With this background it is then possible to predict whether a water will be aggressive to cement type materials and to what extent. Methods used to assess the extent of "aggressiveness" via the saturation state are introduced.

3.2 AQUEOUS-GASEOUS PHASE EQUILIBRIUM

Carbon dioxide exchange between water and the atmosphere takes place until the carbon dioxide (CO_2) partial processes in the two phases are equal, i.e. at equilibrium between air and water the dissolved CO_2 concentration is fixed.

In the approach to aqueous-gaseous equilibrium the pH in the water changes and there is a redistribution of the dissolved carbonic concentrations, i.e. a change in the dissolved CO_2 concentration occurs and more CO_2 is exchanged with the air. The pH at which equilibrium is established depends on the Alkalinity of the water. Exchange of CO_2 between air and water does not change the Alkalinity, only the Acidity and pH, provided no $CaCO_3$ precipitation occurs.

For equilibrium between dissolved and atmospheric CO_2 at a particular partial pressure of CO_2 ($\bar{p}CO_2$) the concentration of dissolved CO_2 is defined by Henry's Law as :

$$[H_2CO_3^*] = K_{CO_2} \cdot \bar{p}CO_2 \qquad (3.1)$$

$$pK_{CO_2} = -1760{,}0/T + 9{,}619 - 0{,}00753T \qquad (3.2)$$

$$= 1{,}407 \text{ at } 20°C.$$

where K_{CO_2} is Henry's Law Constant which is temperature dependant

$\bar{p}CO_2$ is the partial pressure of CO_2 in the atmosphere

T is temperature in Kelvin.

For CO_2 equilibrium between a constant partial pressure of CO_2 in the atmosphere and water, Alkalinity and pH are directly related as follows :

From Equation (2.6)

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH] - [H]$$

solving for $[CO_3^{2-}]$ and $[HCO_3^-]$ from Equations (2.2 and 2.3) respectively and substituting into the equation above for Alkalinity,

$$\text{Alkalinity} = [H_2CO_3^*] \cdot 10^{pH-pK_1'} (2.10^{pH-pK_2'} + 1) + 10^{pH-pK_w'} - 10^{-pH} / F_m$$

and substituting for $[H_2CO_3^*]$ from Equation (3.6)

$$\text{Alkalinity} = \bar{p}CO_2 \cdot K_{CO_2} \cdot 10^{pH-pK_1'} (2.10^{pH-pK_2'} + 1) + 10^{pH-pK_w'} - 10^{-pH} / F_m \qquad (3.3)$$

Thus, from Equation (3.3) Alkalinity is directly related to pH for a water at equilibrium with CO_2 in the air. Equilibrium between carbonate species in the aqueous phase and CO_2 in the gaseous phase (say air with $\bar{p}CO_2$ = 0,00032 Atmospheres) can be depicted in a Modified Caldwell-Lawrence diagram (see below in Section 3.4) allowing for quick graphical assessment of whether aqueous-gaseous equilibrium exists in a water.

3.3 AQUEOUS-SOLID PHASE EQUILIBRIUM

When a mineral dissolves in water, the mass which can dissolve per unit volume of liquid is limited. This limiting concentration is termed the solubility of the mineral in the particular liquid. Of importance to this investigation is the solubility of the various calcium salts, in particular calcium carbonate and to a lesser extent calcium hydroxide (lime). The solubility status of transported water with regard to these minerals will determine whether aggressive attack of cement concrete conduits occurs. Assessment of the solubility status is achieved by considering the water saturation state.

Undersaturation, supersaturation and saturation are terms describing whether the chemical state of a water is respectively such that it causes dissolution of a solid (undersaturation), precipitation of a solid (supersaturation), or no precipitation or dissolution (saturation). Aggressive waters attack cement type pipes and structures by dissolving free lime and $CaCO_3$ from the solid into the aqueous phase giving rise to so called aggressive attack. Such waters are undersaturated with respect to both lime and $CaCO_3$. Chemically these waters are characterised as being "undersaturated" with respect to $CaCO_3$. For waters saturated or supersaturated with respect to $CaCO_3$, solid $CaCO_3$ will not dissolve and free lime in the cement in contact with the water will be transformed with time to solid $CaCO_3$ (see later). For this reason the solubility status of the water with respect to $CaCO_3$ is of crucial importance whilst that of the considerably more soluble lime is not crucial.

Theoretically, the saturation state with respect to $CaCO_3$ is identified by comparing the activity product of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species with the solubility product constant, K_{sp}. The activity product is the product of the active molar concentration of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species, i.e.

$$\text{Activity Product} = (Ca^{2+})\,(CO_3^{2-}) \tag{3.4}$$

The activity product cannot increase *ad lib* but has a stable upper limit called the <u>solubility product</u>.

If the activity product is greater than the solubility product constant, K_{sp}, precipitation of solid calcium carbonate out of the water occurs; if less, dissolution of solid calcium carbonate into the water takes place; if equal, there will be no net dissolution or precipitation.

Hence, for dissolution of calcium carbonate (undersaturation),

$$(Ca^{2+})\,(CO_3^{2-}) < K_{sp} \tag{3.5a}$$

For precipitation of calcium carbonate (supersaturation),

$$(Ca^{2+})\ (CO_3^{2-}) > K_{sp} \qquad (3.5b)$$

and, at saturation,

$$(Ca^{2+})\ (CO_3^{2-}) = K_{sp} \qquad (3.5c)$$

Where K_{sp} = thermodynamic solubility product constant
$(\ )$ = "active" concentration of the ion.

In Equations (3.5 a, b and c), K_{sp} is the thermodynamic solubility product for calcium carbonate. The value of the thermodynamic solubility product depends on temperature, pressure and the type of calcium carbonate mineral precipitated (e.g. calcite, aragonite or vaterite). The type of mineral that will precipitate depends on the ionic constitution of the water (i.e. the concentration and types of salt present in solution), state of supersaturation, temperature and pressure. For low ionic strength waters in the temperature 0-60°C, at low degrees of supersaturation and atmospheric pressure, the usual calcium carbonate mineral that will precipitate, is calcite (Loewenthal and Marais, 1976). The calcite solubility product is temperature dependent as follows (Loewenthal and Marais, 1976) :

$$pK_{sp} = 0{,}01183\ t + 8{,}03 \qquad (3.6)$$
$$= 8{,}266 \text{ at } 20°C$$

where $pK_{sp} = -\log_{10} K_{sp}$
t = temperature in degrees celsius.

In Equation (3.5) the "active concentrations" of the ions, (Ca^{2+}) and (CO_3^{2-}) are effective concentrations, not the stoichiometric concentrations. The effective concentrations (or activities) are related to the stoichiometric concentrations through activity coefficients, i.e.

$$(Ca^{2+}) = F_d\,[Ca^{2+}]$$

where (Ca^{2+}) = activity

$[Ca^{2+}]$ = stoichiometric concentration (moles/ℓ)

F_d = activity coefficient for a divalent ion.

$$\text{i.e.}\quad (Ca^{2+})\,(CO_3^{2-}) = F_d\,[Ca^{2+}]\,F_d\,[CO_3^{2-}] \qquad (3.7)$$

The righthand side of Equation (3.7) is more useful in practical work as measurements are usually stoichiometric. Consequently, for saturation,

$$[Ca^{2+}]\,[CO_3^{2-}] = K_{sp}/F_d^2 = K'_{sp} \qquad (3.8)$$

where K'_{sp} = apparent solubility product for $CaCO_3$.

To utilize Equation (3.8) in the estimation of the saturation state requires quantitive values for $[CO_3^{2-}]$, $[Ca^{2+}]$, K_{sp} and F_d. The concentrations $[Ca^{2+}]$ and $[CO_3^{2-}]$ are stoichiometric quantities which are measured either indirectly (i.e. $[CO_3^{2-}]$ using Equations (2.1 to 2.3) or directly (i.e. $[Ca^{2+}]$). K_{sp} is determined from Equation (3.8) while the activity coefficient, F_d, is readily estimated for low salinity waters for a known ionic strength as set out in Appendix A.

In order to assess the saturation state with respect to calcium carbonate one needs to determine from some series of measurements the concentrations of dissolved calcium and carbonate (CO_3^{2-}) species. Methods for measuring calcium are well set out in the literature (*inter alia*, Standard Methods, 1985), however, determination of the concentration of dissolved carbonate species (i.e. CO_3^{2-}) cannot be carried out directly and must be determined indirectly from other "measurements". In this regard it was shown in the previous chapter that to characterize the aqueous phase two measurements are required, for example: if pH and Alkalinity are measured CO_3^{2-} concentration can be determined via the equilibrium and mass balance expressions. However, such calculations are tedious and time-consuming. As a result various semi-empirical methods for assessing the saturation state have been developed (see Section 3.5). However, the majority of these will indicate only whether a water is super, under or just saturated and give no indication of the potential mass concentration of $CaCO_3$ which can dissolve or precipitate. A rapid method for assessing this potential based on equilibrium chemistry is via a graphical description of the carbonate system depicting both single aqueous phase equilibrium and aqueous-solid phase equilibrium (and also aqueous-solid-gaseous phase equilibrium, i.e. 3 phase). These graphical descriptions are effected in a Modified Caldwell-Lawrence Diagram (see Section 3.4 below). Use of the diagram for quantifying aggressiveness of waters is carried out in Section 3.5. A brief review of the characteristics of this diagram at equilibrium are in order at this stage.

3.4 THE MODIFIED CALDWELL-LAWRENCE DIAGRAM

The Modified Caldwell-Lawrence (MCL) diagram is a multiphase diagram for carbonate species in the aqueous, solid ($CaCO_3$) and gaseous (CO_2) phases, i.e. it can be used for single aqueous phase considerations as well as aqueous-solid phase, aqueous-gas phase and aqueous-solid-gas phase considerations. The diagram has coordinate parameters Acidity and (Alkalinity-Calcium). Families of curves representing both pH and Alkalinity, and Ca^{2+} values at saturation with respect to $CaCO_3$ are superimposed in the diagram. Each diagram is for a water with a particular temperature and ionic strength, a typical example being shown in Figure 3.1. (The theory for constructing the MCL diagram is set out in detail by Loewenthal and Marais (1976)).

<u>Single aqueous phase</u> problems are resolved using lines representing Alkalinity, Acidity and pH and as such the MCL diagram constitutes a single phase conditioning chart. If lines representing values for any two of these three parameters are plotted on this diagram, the intersection point quantifies the third parameter. For example, in

Figure 3.1; if Alkalinity equals 95 mg/ℓ as $CaCO_3$, pH = 8,2 then Acidity = 97 mg/ℓ as $CaCO_3$. The MCL can also be used to assess changes in state with chemical dosing as follows :

(i) Lines are plotted in the MCL diagram representing the measured initial Alkalinity and pH values. The initial Acidity is then determined from the Acidity ordinate intersection point of the Alkalinity and pH lines.

(ii) The new Alkalinity and Acidity are determined from the mass concentration of chemical added (or removed) using Equations 2.18 and 2.19 respectively.

(iii) The new pH is determined from the intersection of the lines representing the new Alkalinity and Acidity values (determined in (ii) above).

In addition, to use as an aqueous phase conditioning diagram, the MCL diagram can be used for <u>aqueous-gaseous phase</u> considerations. Equilibrium between carbonate species in the aqueous phase and CO_2 in the gas phase can be depicted in the MCL diagram as follows :

(i) For water of a particular temperature and ionic strength determine values for the apparent constants, K_1' and K_2' and K_w' (as set out in Appendix A) and for K_{CO_2} from Equation (3.2).

(ii) For a range of pH values (and $\bar{p}CO_2$ equals, say, 0,00032 Atm) determine the corresponding Alkalinity values using Equation (3.3).

(iii) In the MCL diagram plot the points representing corresponding pH and Alkalinity values. A line joining these points represents the condition for equilibrium between carbonate species in solution and CO_2 in the air (see Line A in Figure 3.1). A water whose condition plots on Line A is at equilibrium with CO_2 in the air. If not, then CO_2 is expelled or taken up by the water until two phase equilibrium is attained.

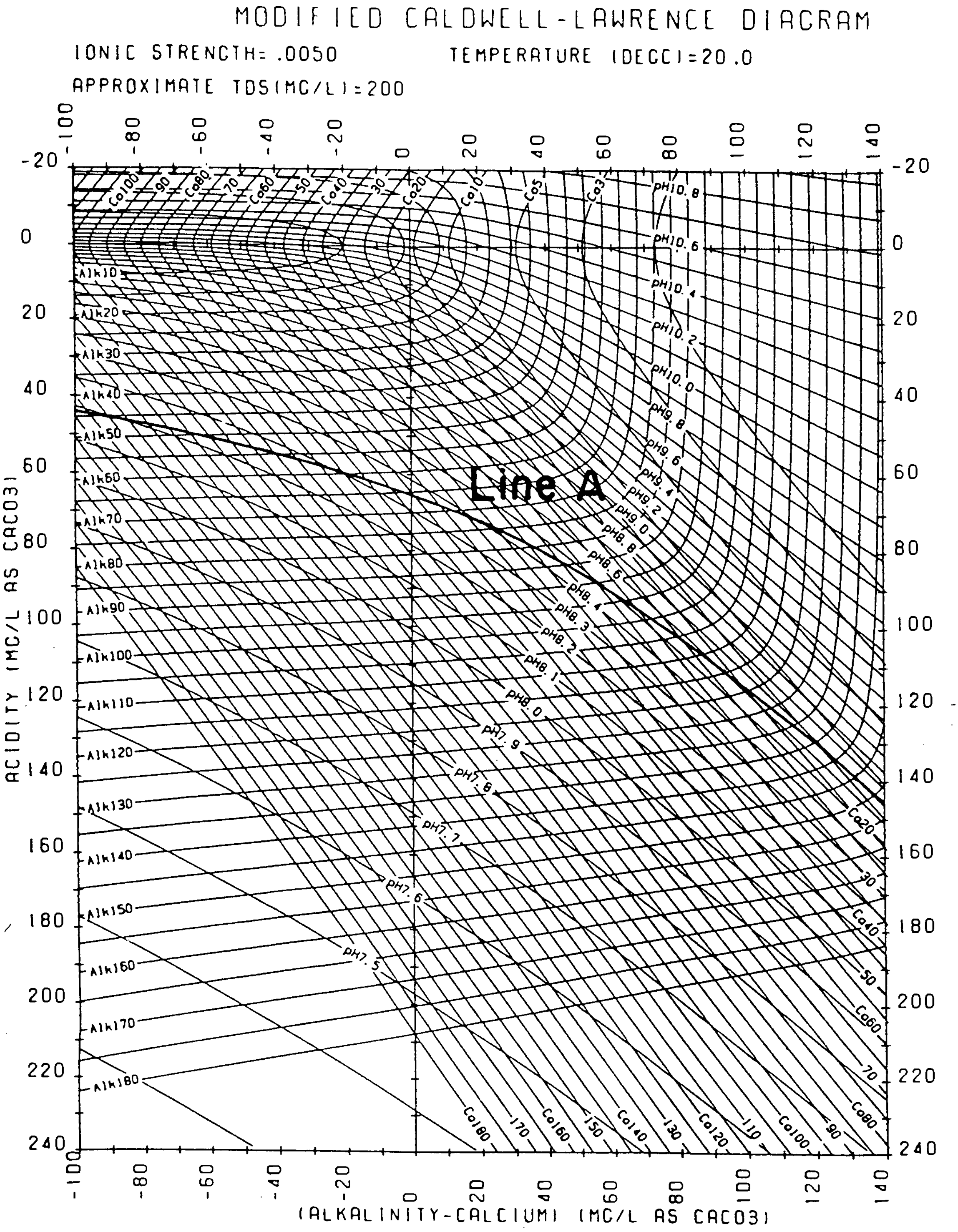

Figure 3.1 : **Modified Caldwell-Lawrence diagram.**

The MCL diagram has a further additional advantage over the single phase Deffeyes type diagram (introduced in Section 2.5) that it also gives a description of the saturation state of water with respect to $CaCO_3$.

To assess the $CaCO_3$ saturation state, i.e. whether or not equilibrium exists between species in the aqueous and solid phases, lines representing measured values for pH, Alkalinity and Ca^{2+} are plotted. If these lines intersect at a single point the water is just saturated with respect to $CaCO_3$, if not, it is either super- or under-saturated. Which of these two states exists is rapidly determined by comparing the measured Ca^{2+} value with value of the Ca^{2+} line passing through the intersection point of observed pH and Alkalinity (i.e. passing through the aqueous phase equilibrium point). If the measured calcium value is higher, the water is super-saturated and precipitation of $CaCO_3$ will occur; if the measured value is lower, the water is under-saturated and dissolution of $CaCO_3$ into the water can be expected. Having identified the saturation state of the water the next logical step would be to calculate the potential for dissolution or precipitation of $CaCO_3$, i.e. what quantity of $CaCO_3$ will the water take up (if a source is available) or precipitate to reach aqueous-solid phase equilibrium.

3.5 ASSESSING THE $CaCO_3$ PRECIPITATION/DISSOLUTION POTENTIAL OF A WATER

It has been shown that depending on the chemical characteristics of a water it will either effect dissolution of solid $CaCO_3$ (under-saturation), precipitation of $CaCO_3$ (super-saturation) or neither (just saturated). These states describe the aggressiveness of a water; the water being non-aggressive if it possesses a $CaCO_3$ precipitation potential and aggressive if it possesses a $CaCO_3$ dissolution potential. Furthermore, the degree of aggressiveness is linked quantitatively to the $CaCO_3$ dissolution potential.

A number of methods currently are used for determining whether a water is potentially aggressive or not. Amongst these methods those most commonly used are :

(a) Calcium Carbonate Precipitation/Dissolution Potential: this describes both whether a water is aggressive or not and the degree of aggressiveness via the precipitation/dissolution potential.

(b) Langelier Saturation Index: This only describes whether a water is aggressive or not.

(c) Aggressiveness Index: This describes whether a water is aggressive or not and <u>supposedly</u> the degree of aggressiveness.

The Calcium Carbonate Precipitation/Dissolution Potential method is the only truly quantitative and qualitative method of these and will be considered first.

(a) <u>Calcium Carbonate Precipitation Potential</u>

The "precipitation/dissolution potential" is defined as the mass of $CaCO_3$ to be precipitated from, or dissolved into, a water to attain saturation with respect to $CaCO_3$. Consequently this parameter gives both a quantitative and qualitative description of the aggressiveness of a water.

Experimental determination of the precipitation/dissolution potential is carried out using the Marble Test (see Standard Methods, 1985). This involves adding solid $CaCO_3$ to a water sample and measuring the change in calcium content that occurs in 24 hours (it is assumed that this supplies sufficient time for $CaCO_3$ saturation to be attained). However, not only is the test time consuming, but also significant errors may arise due to both carbon dioxide exchange with the gas phase (air) and difficulties in separating the very fine solid phase from the aqueous phase. For these reasons theoretical methods based on equilibrium chemistry have gained popularity.

Theoretical determination of the saturated state and the Calcium Carbonate Precipitation/Dissolution Potential using equilibrium chemistry is carried out very easily either (i) graphically as proposed by Loewenthal and Marais (1976) using the Modified Caldwell-Lawrence (MCL) diagram or, (ii) using user-friendly computer software (Loewenthal *et al*, 1989).[1] In this monograph only the former is discussed.

The MCL diagram has been described briefly in the previous section where it was used for determining the saturation state of a water. Its use can be extended to include *inter alia* determination of the precipitation/dissolution potential (i.e. aggressiveness). A detailed description of its application for this purpose and for the purposes of chemical conditioning are set out by Loewenthal *et al* (1986). Summarized below is the procedure for determining the precipitation/dissolution potential.

(i) Select the MCL diagram with ionic strength and temperature equal to (or close to) those for the water to be assessed.

(ii) Using the selected diagram draw in the lines representing the measured values for pH, Alkalinity and Ca^{2+}.[2] If these three lines do not intersect at a single point the water is in a state of super or under-saturation and precipitation or dissolution of $CaCO_3$ will occur.

(iii) Draw in the horizontal line representing the Acidity of the water: this is given by the Acidity ordinate value of the aqueous phase equilibrium point, i.e. the horizontal line through the intersection of pH and Alkalinity.

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[1] For the use of user friendly software the reader is referred to the package STASOFT. STASOFT is available on request from the Water Research Commission, P O Box 824, Pretoria, S.A.

[2] Note: The diagram is formulated with species concentration on the scale 'mg/ℓ as $CaCO_3$' because this is the usual form of reporting this data in water

(iv) Draw in the vertical line representing the (Alkalinity - Ca^{2+}) value for the water. This will be a vertical line through the intersection point of the lines representing measured Alkalinity and Ca^{2+}.

(v) Identify the final saturated aqueous-solid phase equilibrium state that the water will attain eventually. This is given by the intersection of the Acidity and (Alk - Ca^{2+}). (The reason for this is that with dissolution or precipitation of $CaCO_3$ the ordinate parameters to the diagram remain constant, whereas Alkalinity, Ca^{2+} and pH values all change). The saturated values for Alk, Ca^{2+} and pH that the water will eventually attain equal the respective values of the lines through this saturated equilibrium point.

(vi) The potential mass concentration of $CaCO_3$ to be precipitated or dissolved to saturation is determined either from the difference between the initial and saturated Ca^{2+} values or the difference between the initial and saturated Alkalinity values, i.e.

Precipitation Potential

= Ca^{2+} (initial) - Ca^{2+} (saturated)

= Alkalinity (initial) - Alkalinity (saturated)

If the value of the precipitation is positive the water is super-saturated by this potential; if negative the water is under-saturated by this potential.

<u>Example One</u> : Analysis of a water gives Alkalinity 90 mg/ℓ, Ca^{2+} 10 mg/ℓ (both as $CaCO_3$), pH 8,0, TDS = 100 mg/ℓ, temperature 20°C. The $CaCO_3$ dissolution/precipitation potential is determined as follows (all concentrations are expressed in mg/ℓ as $CaCO_3$) :

(i) Figure 3.2 is selected for the reported ionic strength and temperature.

(ii) Draw in the lines representing Alkalinity, Calcium and pH.

(iii) Draw in the horizontal line representing Acidity, i.e. the horizontal line through the intersection point of measured Alkalinity and pH, Acidity = 93 mg/ℓ.

(iv) Draw the vertical line representing (Alk - Ca^{2+}), i.e. (90-10) = 80 mg/ℓ (or simply draw in the vertical line through the intersection point of the lines representing measured Alkalinity and Calcium values).

(v) The plotted ordinate values for (iii) and (iv) above intersect at point 1 in Figure 3.2. This is the final saturated aqueous-solid phase equilibrium state that the water will attain eventually (if in contact with solid $CaCO_3$). Hence at saturation the Alkalinity, Ca^{2+} and pH values are given by the values of the lines representing these parameters and passing through point 1, i.e.

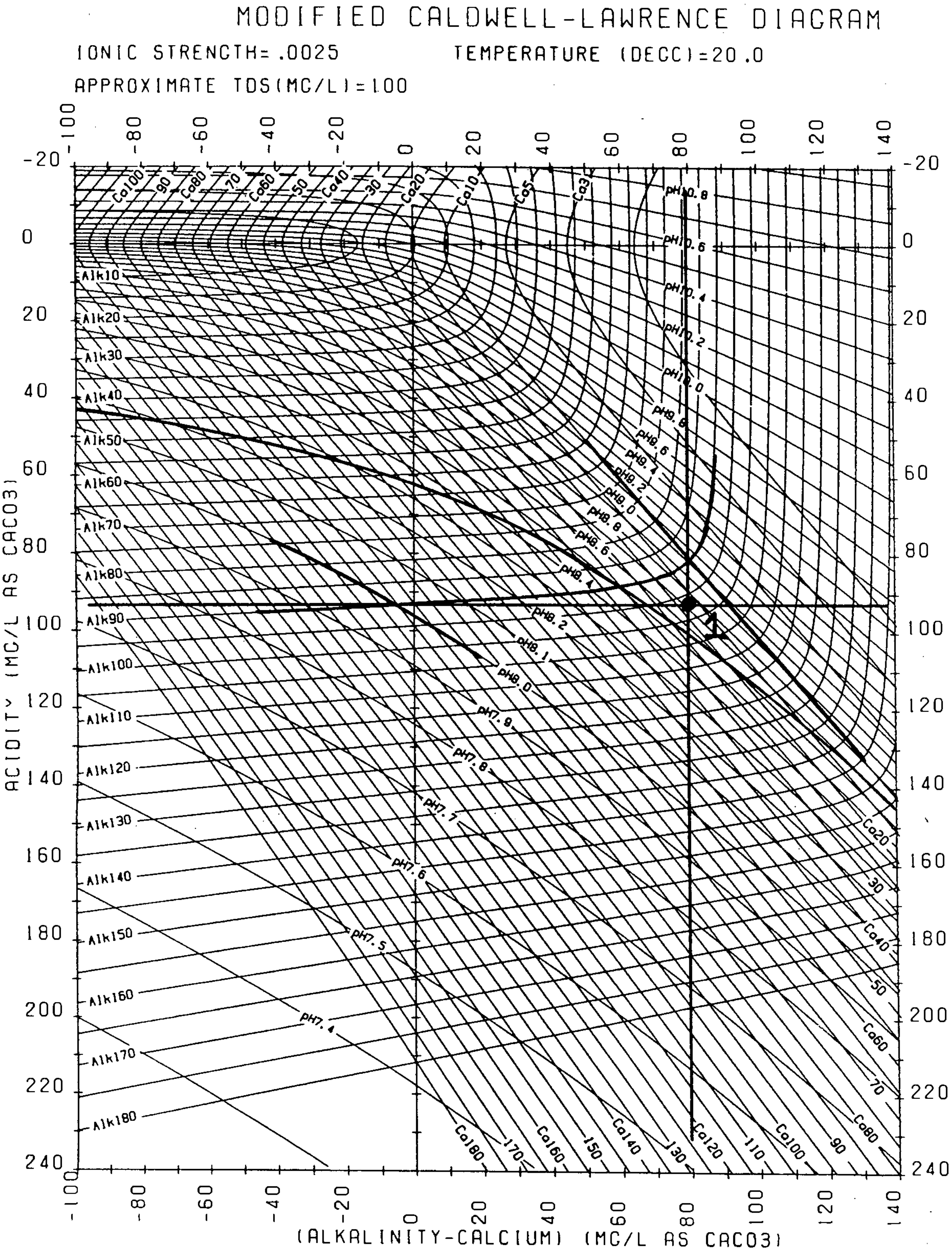
Alkalinity (sat) = 97 mg/ℓ
Ca^{2+} (sat) = 17 mg/ℓ
pH (sat) = 8,8

(vi) The changes in either Alkalinity or Ca^{2+} give the mass of $CaCO_3$ to be dissolved to saturation, i.e. :

$CaCO_3$ precipitation potential :

$$= (Ca^{2+})\ \text{in} - (Ca^{2+})\ \text{sat} = 10-17 = -7\ \text{mg}/\ell$$

$$= (\text{Alk})\ \text{in} - (\text{Alk})\ \text{sat} = 90-97 = -7\ \text{mg}/\ell$$



<u>Figure 3.2</u> : Example 1 : Determination of $CaCO_3$ dissolution potential for an undersaturated water with Alk 90 mg/ℓ, Ca^{2+} 10 mg/ℓ and pH 8,0.

The negative sign indicates that 7 mg/ℓ of $CaCO_3$ will <u>dissolve</u> to obtain saturation.

When considering low Alkalinity, low pH waters, an extra step will need to be included to solve for aqueous phase equilibrium (i.e. to determine Acidity) due to practical limitations of the MCL diagram. Determination of Acidity is then achieved using a Deffeyes type diagram (see Section 2.5) and thereafter the graphical solution of the precipitation/dissolution potential is unchanged.

<u>Example Two</u> : A typical Western Cape water after colour removal has Alkalinity 2 mg/ℓ, Ca^{2+} 10 mg/ℓ (both as $CaCO_3$), pH 5,9, TDS 40 mg/ℓ, temperature 15°C. the $CaCO_3$ dissolution/precipitation potential is determined as follows. (All concentrations are expressed in mg/ℓ as $CaCO_3$:

(i) Figure 3.3 is selected for the reported ionic strength and temperature.

(ii) In this example we note that the line representing pH = 5,9 does not appear in the diagram (it lies below the lower edge of the chart); similarly, the line representing Alkalinity = 2 mg/ℓ does not appear in the diagram (it lies off the left edge of the chart). Consequently, for this soft acidic water Acidity cannot be determined using an MCL diagram. However, it can be determined using Deffeyes type diagram (see Section 2.5), Figure 3.4.

Referring to the Deffeyes type diagram, Figure 3.4, plot in the lines representing pH = 5,9 and Alkalinity = 2, these intersect at point 2. Acidity is then given by the Acidity ordinate value of point 2, i.e.

$$\text{Acidity} = 15 \text{ mg/}\ell$$

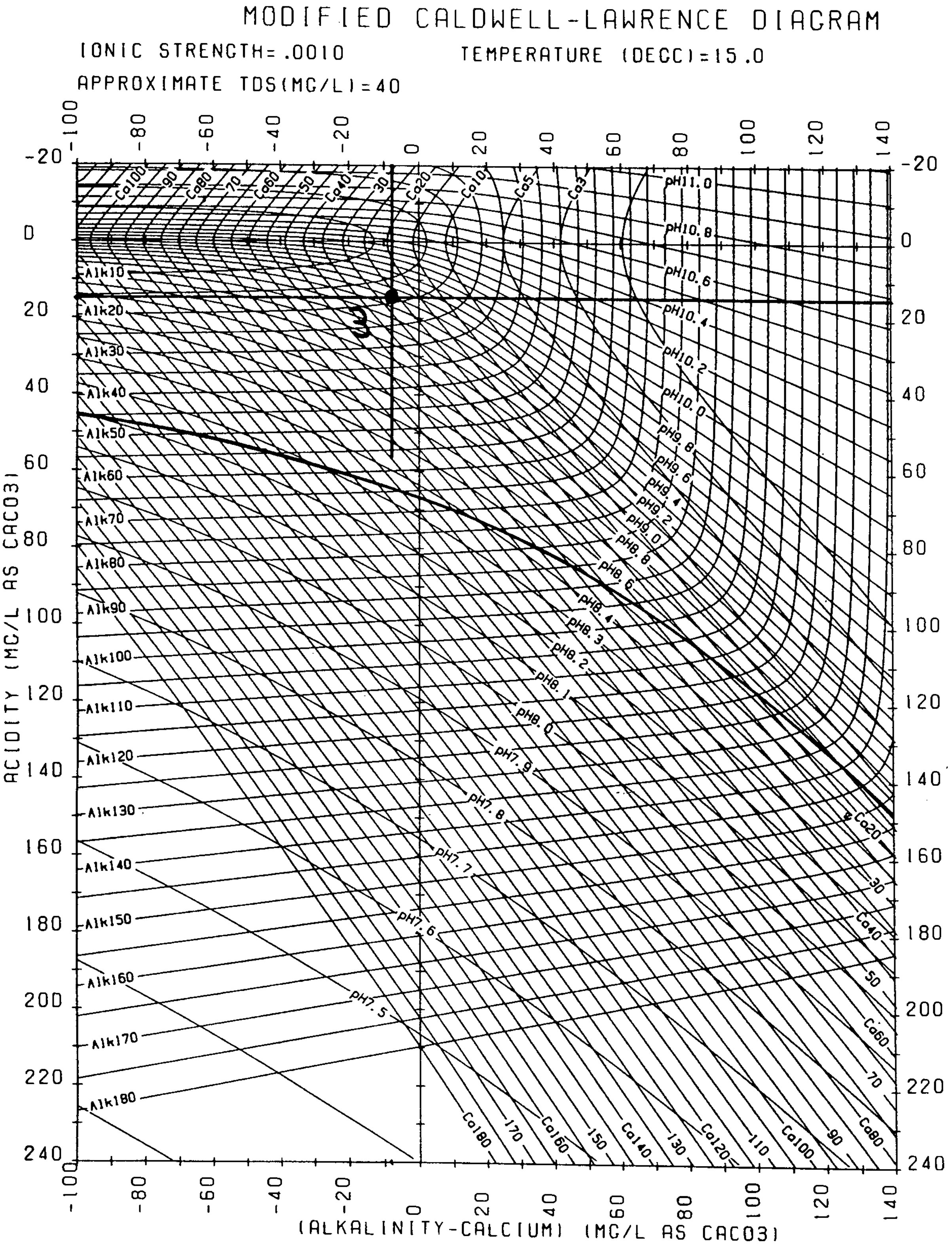


Figure 3.3 : Example 2 : Determination of $CaCO_3$ dissolution potential for an undersaturated water with Alk 2,0 mg/ℓ,

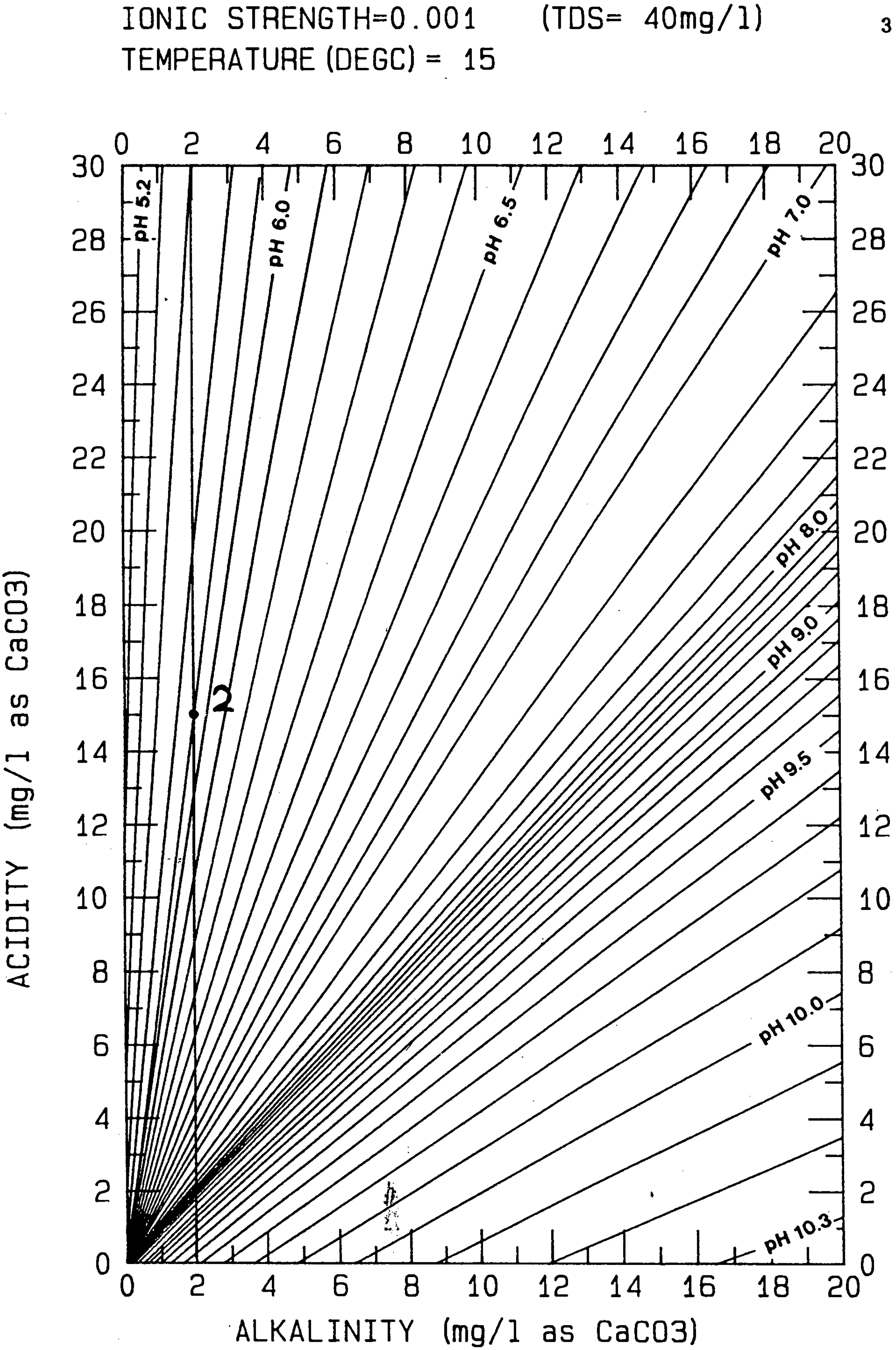


Figure 3.4 : Example 2 : Use of Deffeyes type diagram to determine Acidity, Alkalinity 2 mg/ℓ and pH 5,9, gives Acidity

(iii) Draw in the horizontal line representing Acidity = 15 mg/ℓ in the MCL diagram, Figure 3.3.

(iv) Draw the vertical line representing (Alk - Ca^{2+}) i.e.

$$(2-10) = -8 \text{ mg}/\ell$$

(v) The plotted ordinate values from (iii) and (iv) above intersect at point 3 in Figure 3.3. This is the final saturation aqueous-solid phase equilibrium state that the water will eventually attain if in contact with $CaCO_3$. Hence, at saturation the Alkalinity, Ca^{2+} and pH values are given by the values of the lines representing these parameters and passing through point 3, i.e.

Alkalinity (sat) = 18
Ca^{2+} (sat) = 26
pH (sat) = 9,4

(vi) The changes in either Alkalinity or Ca^{2+} give the mass of $CaCO_3$ to be dissolved to saturation, i.e.

$CaCO_3$ precipitation potential
$= (Ca^{2+})\text{ in} - (Ca^{2+})\text{ sat} = 10-26 = -16 \text{ mg}/\ell$
$= (Alk)\text{ in} - (Alk)\text{ sat} = 2-18 = -16 \text{ mg}/\ell$

The negative sign indicates that 16 mg/ℓ of $CaCO_3$ will <u>dissolve</u> to obtain saturation.

The examples above show that the MCL diagram (and for low pH, low Alkalinity waters, the Deffeyes diagram) give both a quantitative and qualitative description of a water enabling one to determine its aggressiveness to cement type materials.

(b) Langelier Saturation Index

In 1936 Langelier developed what is historically the most important attempt to establish whether a water is aggressive or non-aggressive. Langelier recognised that if Alkalinity, pH and calcium concentration of a water are measured it is then possible to calculate whether a water is under-, super- or just saturated with respect to $CaCO_3$.

To determine this easily he developed the Langelier Saturation Index (S.I.) as follows :

For a measured Alkalinity and calcium there is a pH at which the water is just saturated with respect to $CaCO_3$. This theoretical pH he termed the saturation pH, pH_s. The S.I. is then defined as $(pH_{actual} - pH_s)$. If the index is zero, the water is just saturated; if positive, the water has a tendency to precipitate $CaCO_3$; if negative, to dissolve $CaCO_3$ and be aggressive to cement materials.

Langelier proposed determination of the S.I. from measurement of pH and Alkalinity and calcium concentrations as follows :

$$SI = pH_{actual} - pH_s \tag{3.9}$$

$$pH_s = (pK_2' - pK_{sp}') + p\,[Ca^{2+}] + p\,[Alk] \tag{3.10}$$

where pH_{actual} = measured pH of the water

pH_s = theoretical pH for $CaCO_3$ saturation for the measured Alkalinity and Calcium concentration of the water, and, in the region $6 < pH < 9$.

[ ] = molar concentration

K_2' and K_{sp}' = apparent equilibrium constant as defined in Equations 2.3 and 3.8.

pX = $\log_{10}X$.

Equation 3.10 for pH_s is developed from equilibrium equations. In effect this equation is formulated by assuming the water to be just saturated with $CaCO_3$ for the measured Ca^{2+} and Alkalinity values and determining the required pH, i.e. pH_s. Implicit in the formulation is the assumption that Alkalinity equals HCO_3^- species concentration; this assumption is reasonably only in the region $6,0 \leq pH \leq 9,0$. (An in-depth discussion on the development of Equation 3.10 for pH_s is given by Loewenthal and Marais (1976)). Once pH_s has been determined via Equation 3.10 the S.I. is then determined as the difference between pH_s amd the observed pH, i.e. Equation 3.9.

Determination of both pH_s and the S.I. can be conveniently depicted in the MCL diagram. For example : analysis of a water gives Alkalinity 40 mg/ℓ, Ca^{2+} 30 mg/ℓ (both as $CaCO_3$) and pH 9,6.

Using Figure 3.2 plot in the lines for Alkalinity = 40 and Ca^{2+} = 30; these intersect at a single point. The value of the pH line through this point gives pH_s i.e. pH_s = 9,15. We note that pH is greater than pH_s, and from Equation 3.9

$$\begin{aligned} S.I. &= 9{,}6 - 9{,}15 \\ &= +\,0{,}45 \end{aligned}$$

The positive sign for S.I. indicates the water is super-saturated. This graphical description clearly illustrates that Langelier's pH_s is only a theoretical concept and certainly does not reflect the final saturated pH which a water will attain. In the example above the true saturated pH which the water will attain is given by the pH value through point 5, i.e. pH = 9,3. As can be seen, the pH reached, which satisfies aqueous-solid phase equilibrium, is not pH_s.

A more important deficiency of the index is that it does not reflect the degree of aggressiveness. This is illustrated by noting that waters with the same S.I. but different initial pH, Alkalinity and calcium will not necessarily precipitate out or dissolve the same amount of $CaCO_3$ to reach aqueous-solid phase equilibrium. This is due to the varying capacity with pH and Alkalinity (Loewenthal *et al*, 1986). Table 3.1 lists the mass of $CaCO_3$ to be precipitated to saturation (determined from the MCL diagram) for a number of waters with the same S.I. but with varying Alkalinity, Ca^{2+} and pH values.

In conclusion, these observations emphasize that the S.I. can be used only for qualitative and not quantitative assessments of a water's characteristics with regard to aggression.

TABLE 3.1 : Mass concentration of $CaCO_3$ that precipitates to saturation for a number of waters each with a Langelier Saturation Index of +0,3 (all concentrations mg/ℓ as $CaCO_3$)

pH	Alkalinity	Ca^{2+}	SI	$CaCO_3$ precipitation potential
7,3	300	460	+ 0,3	35
7,9	188	190	+ 0,3	8
8,4	95	95	+ 0,3	2
9,0	65	19	+ 0,3	5
9,3	38	40	+ 0,3	3

(c) Aggressiveness Index

In an attempt to quantify the aggressiveness of a water the AWWA (Standard C400-77, 1977) introduced the Aggressiveness Index (AI) (Millette *et al*, 1980) as :

$$AI = pH + \log_{10} \{Alk\ Ca^{2+}\} \tag{3.11}$$

where Alk = Alkalinity in mg/ℓ as $CaCO_3$
Ca^{2+} = calcium concentration in mg/ℓ as $CaCO_3$
pH = measured pH of the water

and classified the aggressiveness of water as follows :

1.	$AI \leq 10,0$	Highly aggressive
2.	$10,0 \leq AI \leq 11,9$	Moderately aggressive
3.	$AI \geq 12,0$	Non-aggressive.

The equation for the AI, Equation 3.11, is developed by taking the logarithm of the stoichiometric product of Ca^{2+} and CO_3^{2-} concentrations (both in mg/ℓ as $CaCO_3$) in the water. The CO_3^{2-} concentration, which cannot be measured directly, is formulated in terms of Alkalinity and pH, from Equation 2.3, as :

$$[CO_3^{2-}] = \frac{K_2' \, [HCO_3^-]}{(H)}$$

where the value for $[HCO_3^-]$ is assumed equal to Alkalinity (the equation is therefore only valid in the region $6,0 \leq pH \leq 9,0$ where the assumption regarding Alkalinity is acceptable). Taking the logarithm of the stoichiometric product yields the following :

$$\begin{aligned} \log\,[Ca^{2+}]\,[CO_3^{2-}] &\simeq \log\,[Ca^{2+}] + \log\,[CO_3^{2-}] \\ &\simeq \log\,[Ca^{2+}] + \log\,[Alk] + pH + \log K_1' \end{aligned}$$

rearranging terms,

$$pK_1' + \log\,[Ca^{2+}]\,[CO_3^{2-}] \simeq pH + \log_{10}\,[Alk]\,[Ca^{2+}]$$

where K_1' = apparent equilibrium constant as defined in Equation 2.2

pH = measured pH of the water

[ ] = molar concentration

pX = $- \log_{10}X$

Converting the concentration scale to mg/ℓ as $CaCO_3$ gives

$$pK_1' + \log_{10}10^6 + \log_{10}[Ca^{2+}][CO_3^{2-}]$$
$$\simeq pH + \log_{10}\{Alk.Ca^{2+}\}$$

(Where the use of no brackets indicates that species concentration and Alkalinity are expressed in mg/ℓ as $CaCO_3$).

At saturation for a water with temperature 20°C and infinite dilution the lefthand side of Equation 3.11 reduces to

$$\begin{aligned} LHS &= pK_1 + \log_{10} 10^6 + \log K_{sp} \\ &= 11{,}81 \end{aligned}$$

where K_{sp} = thermodynamic solubility product constant for $CaCO_3$ as defined in Equation 3.4.

The righthand side of Equation 3.11 is defined as the AI and is to be determined from measured characteristics of a water. If, in the instance of a water with temperature 20°C and infinite dilution, the AI is less than 11,81 the water is undersaturated with respect to $CaCO_3$ and dissolution of solid $CaCO_3$ will occur; conversely, if the AI is greater than 11,81 the water is supersaturated and precipitation of solid $CaCO_3$ out of the water will occur.

Although the AI is easily determined its practical value is questionable for the following reasons :

(i) The AI does <u>not</u> give a quantitative description of precipitation/dissolution potential, and consequently does not quantify aggressiveness, for exactly the same reason as the Langelier saturation index explained earlier. This is illustrated in Table 3.2 by comparing the true $CaCO_3$ dissolution potential for two waters with the same AI, temperature and ionic strength (but different Ca^{2+}, Alkalinity and pH values).

(ii) It does not take into account variations in either ionic strength or temperature, both of which influence equilibrium constant and hence the reference values given to describe aggressiveness.

In conclusion, the AI, like the SI, can only be regarded as useful for an approximate qualitative indication of over or super-saturation.

It has been shown above that use of the Calcium Carbonate Precipitation/Dissolution Potential method is preferable to both the Langelier Saturation Index and the Aggressiveness Index for quantitatively determining the aggressiveness of a water. Pertinent to this thesis is the monitoring and interpretation of changes to an aggressive water's chemical characteristics as dissolution of cement materials takes place. In order to correctly interpret these changes an understanding of the dissolution process is necessary.

TABLE 3.2 : Mass concentration of $CaCO_3$ that dissolves to saturation for two waters each with an Aggressiveness Index of 11,0 (all concentrations mg/ℓ as $CaCO_3$)

	pH	Alk	CA^{2+}	AI	True $CaCO_3$ Dissolution Potential
Water A	8,2	60	10,5	11,0	14,5
Water B	9,8	30	0,5	11,0	6,5

3.6 BEHAVIOUR OF CEMENT-TYPE MATERIALS IN CONTACT WITH AGGRESSIVE AND NON-AGGRESSIVE WATER

When water is in contact with cement concrete one finds either dissolution of calcium compounds from the mortar, or exchange of hydroxide from the mortar with aqueous phase carbonate species, or precipitation of $CaCO_3$ from the water onto the cement surface. Which of these occurs depends on both the $CaCO_3$ saturation state of the water and whether the surface layer of the cement material is carbonated or not. The effects of each of the possible various combinations of these two factors are now considered.

(a) An undersaturated water in contact with an uncarbonated surface : When an undersaturated water is in contact with an uncarbonated surface the dissolution process proceeds with the soluble calcium hydroxide being leached from the cement paste (Muller, 1978). Both the Ca^{2+} and OH^- species go into solution resulting in an increase in Ca^{2+} concentration, Alkalinity and pH of the bulk water. The dissolution of $Ca(OH)_2$ under these conditions can be represented stoichiometrically as :

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (3.12)$$

Continued leaching will eventually result in the decomposition of hydrated calcium silicates and calcium aluminates to provide more $Ca(OH)_2$ for the process (Muller, 1978). In this manner progressive decomposition of the current binder takes place so that eventually all the hardened cement can be decomposed leaving only a residue of aggregate and hydrates of silica, iron and alumina.

(b) An undersaturated water in contact with a carbonated surface :

When an undersaturated water is in contact with a carbonated surface the dissolution process will proceed with the soluble calcium carbonate being leached from the cement paste into the waterbody. Both the Ca^{2+} and $CO_3{}^{2-}$ species go into solution resulting in an increase in Ca^{2+} concentration, Alkalinity and pH of the water (Mills, 1984).

The dissolution of the $CaCO_3$ layer can be represented stoichiometrically as :

$$CaCO_3 \rightarrow Ca^{2+} + CO_3{}^{2-} \qquad (3.13)$$

Once the surface layer of $CaCO_3$ has been dissolved the soluble $Ca(OH)_2$ will be exposed and the dissolution process will proceed as in (a) above.

(c) A saturated (or supersaturated) water in contact with an uncarbonated surface :

When a saturated (or supersaturated) water is in contact with an uncarbonated surface aqueous phase carbonation of the cement material occurs. Initially the more soluble $Ca(OH)_2$ goes into solution immediately resulting in supersaturation of the water body with respect to $CaCO_3$ at the cement surface. Concomitant precipitation of $CaCO_3$ takes place sealing off the uncarbonated cement surface from the bulk water body and thereby preventing further dissolution. In effect, this aqueous phase carbonation can be described as the exchange of dissolved carbonate species with hydroxyl ions. Which of the dissolved carbonate species will participate in the variation of $CaCO_3$ will depend on the water body's chemical characteristics. These reactions can be described stoichiometrically as :

$$Ca(OH)_2 + H_2CO_3^* \rightarrow CaCO_3 + 2H_2O \qquad (3.14)$$

$$Ca(OH)_2 + HCO_3^- \rightarrow CaCO_3 + OH^- + H_2O \qquad (3.15)$$

$$Ca(OH)_2 + CO_3^{2-} \rightarrow CaCO_3 + 2OH^- \qquad (3.16)$$

However, as far as the characteristics of the water are concerned, all the above reactions lead to the same change in state, i.e. a decrease in acidity of 2 molar units and zero change in Alkalinity.

(d) <u>A saturated (or supersaturated) water in contact with a carbonated surface</u> :

If the surface of the cement concrete is carbonated and the water is just- or supersaturated, dissolution of $CaCO_3$ will not take place. The cement material is effectively inactive as chemical equilibria are satisfied. However, although the integrity of the conduit material will be preserved, if the conduit is a pipe and the water is significantly supersaturated, excessive pipe narrowing will occur with time as $CaCO_3$ precipitation takes place. Under these conditions it is likely that, unlike the precipitation in (c) above which takes place at the cement face, precipitation will take place in the bulk water body (Kunzler and Schwenk, 1986).

The precipitation of $CaCO_3$ out of the supersaturated water body can be stoichiometrically described as :

$$Ca^{2+} + H_2CO_3 + 2OH^- \rightarrow CaCO_3 + 2H_2O \qquad (3.17)$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \qquad (3.18)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (3.19)$$

In this investigation attention is given to undersaturated (aggressive) waters in contact with both carbonated and non-carbonated cement type surfaces, i.e. attention is focussed on conditions (a) and (b) above.

The waters investigated are local soft, acid brown humic waters and distilled water. The former contains significant concentrations of dissolved organic acids, the behavioural characteristics of which influence the chemical reactions which take place during dissolution (Robertson and Rashid, 1976). As their influence can be significant and can complicate the reactions which take place during dissolution the following chapter is a brief literature review on relevant aspects of brown waters.

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SECTION A

CHAPTER 4

BROWN HUMIC WATERS

4.1 INTRODUCTION

In Chapter 3 it was shown how waters undersaturated with respect to $CaCO_3$ attack cement type materials by causing dissolution of calcium compounds from the cement matrix. Furthermore, it was shown how equilibrium chemistry can be used to quantify the potential aggression of waters with mineral acidity via the MCL diagram. However, acidity arises in natural terrestrial waters not only from mineral acids (e.g. carbonic and silicic acids) but also organic acids (e.g. humic and fulvic acids). Both of these forms of acidity are pertinent when considering brown humic waters.

Terrestrial waters of the Southern and South Eastern seaboard region of South Africa contain both mineral acidity and organic acidity (the organic acidity arising from dissolved organic substances). The presence of the dissolved organic material associated with organic acidity interferes with equilibrium chemistry considered in Chapter 3 (Gjessing, 1981), making that characterisation of the water, using the usual means of measuring alkalinity and/or acidity and/or pH, is no longer possible. Furthermore, it is known that the organics significantly complex many of the cationic species in the solution (e.g. calcium) making that aggressiveness cannot be quantified due to the concentration of free Ca^{2+} being influenced. As noted in the preamble, conveyance of these waters in concrete conduits has a history of apparent ramdon attack - some systems showing marked attack, others little. Prior to testing the proposed hypothesis that this may be as a result of some conduits having undergone carbonation, a greater understanding of the role played by the dissolved organics present in brown waters is required.

The organic acids present in brown waters are predominantly those that belong to the broad grouping known as humic substances. Humic substances play a leading role in several physical, chemical and geochemical processes in water and sedimentary environments (Baker, 1973; Robertson and Rashid, 1976). Furthermore, these substances can make significant contributions to water acidity as evidenced by pH values as low as 3,0 - 3,4 (Oliver *et al*, 1983). Humic substances are extremely complex and as yet not fully understood. In this chapter a brief discussion of humic substances is followed by consideration of those characteristics of humic substances which will influence aggression.

4.2 BACKGROUND TO AQUATIC HUMIC SUBSTANCES

Brown waters, black waters or humic waters are found in many parts of the world where they are identifiable by their stained yellow to brown colour and low pH values (pH as low as 3,0 - 3,4) (Black and Christman, 1963). In particular, they are common in areas of acid, well leached podsolic soils. Using classical ecological terms these waters are classed as dystrophic and described as acid, brown in colour, low in available nutrients, low in planktonic productivity, low in bacterial numbers, and with depressed benthic and planktonic species richness and abundance (Gardiner, 1989). These features are broad generalisations concerning water bodies which stretch over a wide range of latitudes.

Along the southern and south-eastern seaboard of South Africa the waters that drain the fynbos vegetation (or Cape Macchia) which generally grows on acid well-leached soils, are normally stained to some extent. Cool, second-order, acid, brown stained rivers are typical of the region (Gardiner, 1989). Water colour is, however, greater by orders of recognitude in some of the standing waters, where intensity is high even by international standards. Figure 4.1 (Gardiner, 1990) shows intensity of colour (measured in Hazen units) in south-western Cape vleis contrasted with black and brown waters of other regions in the world.

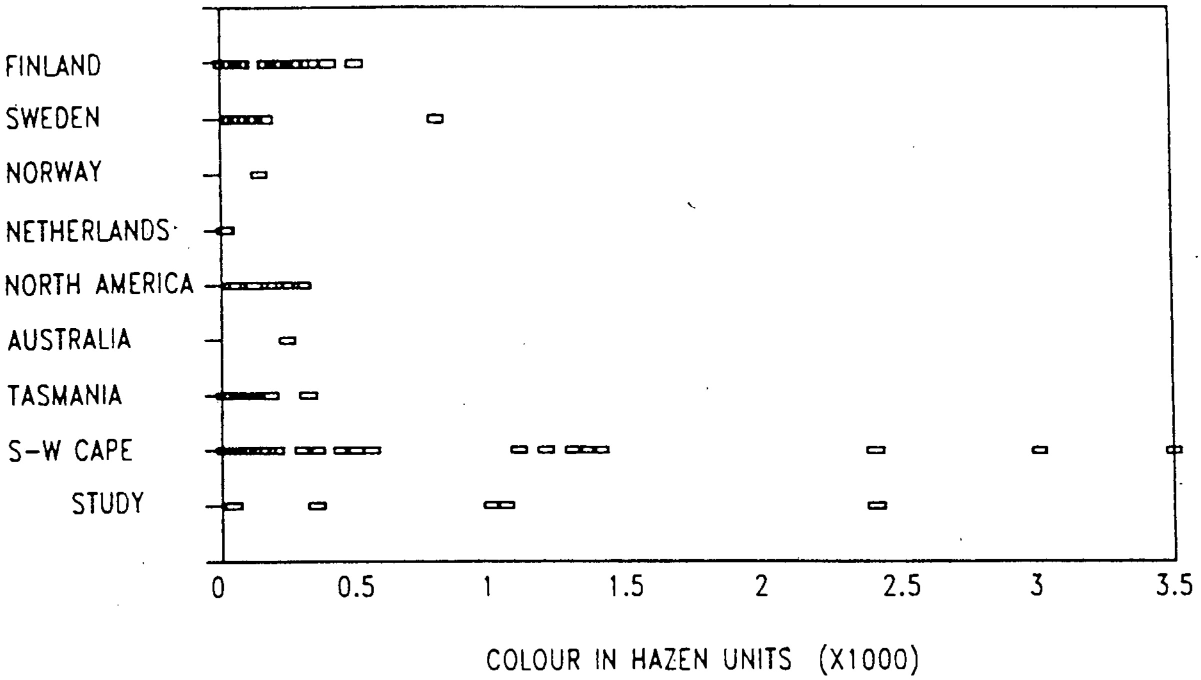

Figure 4.1 : Colour measurements (in Hazen units) from over 130 brownwater or humic lakes in different parts of the world (from Gardiner, 1989).

The compounds which are chiefly responsible for colouring of these waters are collectively termed humic substances. Humic substances are the result of microbial and chemical decomposition of plant material and constitute between 60 and 80% of the dissolved organics present in natural waters (the balance being non-humic substances). Humic substances are comprised mainly of lignins, tannins, carbohydrates and proteins which are all broken down to form the humis molecule. Among these groups of organics lignin is considered to be the most important because carbohydrates and proteins are more available for the soil organisms and have a higher rate of chemical decomposition. The humic substances are thus a combination of macro-molecules having a long formation time (> 50 years) and can be described broadly as amorphous, yellow, brown or black, hydrophilic, acidic, polydisperse, partly aromatic, chemically complex substances (Schnitzer and Kahn, 1972). This broad group can be divided into smaller fractions as follows :

(i) Humic acid which is soluble in dilute alkaline solutions (e.g. 0,5 Na OH) but is precipitated by acidification to pH 2

(ii) Fulvic Acid which is soluble in both acid and base

(iii) Humin which is insoluble.

Aquatic humic substances, i.e. the water extractable fraction of the soil humus, is comprised of the first two fractions. Fulvic acid constitutes the bulk of aquatic humic substances in surface waters, commonly comprising 80 to 90% of the concentration by weight (van Breeman, 1979; Visser, 1984). The molecular weight of humic acid and fulvic acid extracted from natural waters range widely from > 700 to < 26 000 (Gjessing, 1976).

Despite many decades research into humic substances the chemical structure of aquatic humic substances and their behavioural characteristics are still not known with a desirable level of certainty (Liao *et al*, 1982; Choudry, 1981) and no defined chemical and molecular structure has been discovered (*inter alia* Linder and Murray, 1987; Gardiner, 1989). In simple terms the structure of the humic compounds can be described as consisting of a polymeric skeleton or core of varying accounts of aromatic and aliphatic components with attached functional groups. The presence of a wide variety of functional groups is the most characteristic feature of the humic substances, the major functional groups present are the oxygen containing functional groups. (For further information the reader is referred to Schnitzer and Kahn, 1972; Choudry, 1981; and Saar and Weber, 1982). It is through these groups that humic substances react with metals, cations, anions and other organic ligards.

Of importance to this investigation is that aquatic humic substances play an important role in various chemical processes, such as the solubility, mobility, concentrations and accummulation of metals and minerals (Rashid and Leonard, 1973). It is these characteristics which will influence the aggressiveness of brown water to cement concrete materials. The interaction of humic substances with minerals and metals is considered briefly below.

4.3 INTERACTION OF HUMIC SUBSTANCES WITH ENVIRONMENTAL MINERALS AND METALS

When considering the influence that humic substances will have on the aggressiveness of waters to cement type materials it is important to note that although concentrations of humic substances rarely exceed 20 mg/ℓ they are believed to play a significant role in various chemical processes (Rashid and Leonard, 1973). Their ability to form stable complexes with metal ions (Schnitzer and Kahn, 1972) can significantly affect the saturation state and hence stability of minerals (Schnitzer and Kerndorff, 1981).

The most likely mechanism of reaction between humic substances and metal ions is chelation (Schnitzer and Kahn, 1972) in which the metal ions are firmly bonded to organic macro-molecules. Simple cation exchange reactions are also important in metal adsorption phenomena. Both of these mechanisms of metal adsorption enhance the bonding strength of metal ions and organic molecules (Rashid, 1974). These complexes are formed via the various functional groups present on the periphery of the organic molecule (Kerndorff and Schnitzer, 1980), the products being highly stable and soluble organo-metal complexes. Hiratatu (1981) notes that the stability of organo-metal complexes in natural aquatic environments are greater than those of the corresponding inorganic complexes. From these observations it can be expected that the presence of aquatic humic substances will substantially affect the equilibrium chemistry presented in Chapter 2 and 3.

Due to the highly complex and varying nature of the humic substances quantification of their influence on equilibrium chemistry is not presently possible. In particular, it will no longer be possible to quantify aggressiveness. However, a broad general impression of how the humic substances will affect the aggressiveness of water to cement concrete can be obtained via observations in the literature as to their behavioural characteristics.

Reports of both

(a) The influence of humic substances on the solubility of minerals/metals, and

(b) The influence of humic substances on the precipitation of minerals/metals

are presented in the literature. Both of these give an indication of how humic substances will influence aggression and are, therefore, considered below.

(a) The influence of humic substances on the solubility of minerals/metals

Baker (1972) notes that the effectiveness of many naturally occurring organic substances in maintaining the solubility of relatively insoluble inorganic compounds has been demonstrated by numerous investigators in the period 1926 to 1970 and that the powerful solvent action of humic substances in weathering cycles of natural minerals has been reported. Baker compared the solvent activity of five localized North West Tasmanian humic acid towards a number of minerals and metals against that of deionised water equilibrated with atmospheric CO_2 . He found that the humic acid preparation is a strong solvent of many minerals. With all of the minerals studied, the amount of metal extracted is far in excess of that extracted by water. Furthermore, he found that whilst all the humic acids are active in mineral degradation there is considerable variation in the ability of different humic acid to solubilize minerals (see Table 4.1).

Of particular interest to this report is that Ca^{2+} is rapidly removed from calcite to the extent that Baker questions the pernicious effect of humic acid on reinforced concrete piping. Baker further reports that where appreciable metal was mobilized by brown water (Cu, Ni, Mg, Ca) the solution was coloured by the humate indicating that it was the metal complex that was moving.

TABLE 4.1 : Action of various humic acids with minerals and metals (from Baker, 1972)

Sample	Element determined	Water atmos CO_2	µg metal extracted in 1 hour HA 1*	HA 2	HA 3	HA 4	HA 5
Galena	Pb	1	200	210	80	230	110
Sphalerite	Zn	<1	30	90	80	40	30
Bornite	Cu	<1	190	230	180	200	130
Chalcocite	Cu	10	3800	5100	1300	5600	2700
Bismuthinite	Bi	<1	550	1600	410	1000	460
Stibnite	Sb	10	45	340	10	50	<5
Pararammelsbergite	Ni	90	9800	9600	5400	9200	6000
Haematite	Fe	<1	470	90	410	<5	490
Pyrolusite	Mn	1	1000	1800	290	1040	440
Calcite	Ca	50	10500	9600	6400	11100	730
Copper	Cu	<1	5700	5800	3200	6100	4800
Lead	Pb	2	27400	39400	23000	33000	24000

* all extracts 0,1% w/v.

The above observations concerning the ability of humic substances to solubilize minerals are supported by Rashid and Leonard (1973) who investigated modifications in the solubility and precipitation behaviour of various metals in contact with humic acid. He illustrated the importance of humic acid with regard to the solubility of metals by comparing the ability of humic acid and distilled water to solubilize minerals - the quantities of various metals dissolved by humic acid were found to be greater by several magnitudes. The ability of humic substances to solubilize minerals and metals has been reported by many other investigators *inter alia* Rashid, 1974; Gamble *et al*, 1983; Hiratatu, 1981; Schnitzer and Kerndorff, 1981; Saar and Weber, 1982, and is generally accepted.

(b) The influence of humic substances on the precipitation of minerals/metals

The presence of aquatic humic substances in water has been shown in the previous section to play an important role in the solubility of metals. The formation of organo-metal complexes results in the metal ions being unavailable to sulphides, hydroxides, carbonates etc to form insoluble salts, i.e. the solubility product is not reached. One can thus expect that not only will humic substances have the high solvent capabilities described previously but that accordingly they will influence the precipitation of metal ions.

Kitano and Hood (1965) demonstrate that organic compounds such as citrate, malate, pyruvate and glycogen greatly reduced the rate of calcium carbonate precipitation, whilst others affected the rate of formation to a moderate degree.

Rashid and Leonard (1973) noted that organo-metal complexes prevent metals from manifesting their cationic properties and investigated this phenomena by studying precipitation in three anionic media having conditions favourable to yield metal precipitates as carbonates, sulphides and hydroxides. In the carbonate environment they found that 3 to 43 times more metal ions were needed to cause precipitation, whilst in the sulphide environment the quantities of metals required to cause precipitation were 8 to 43 times greater than in the systems that did not contain humic acid. In particular, the precipitation of iron was noted as requiring 40 times more iron. Furthermore, it would appear that not only do the humic substances suppress the cationic properties of metals by complexing but that when crystal growth does take place this is also influenced. Reynolds (1978) states that calcite surfaces adsorb organic matter thereby reducing the surface area of solid in contact with water and consequently slowing or possibly even eliminating precipitation. Reddy (1978) notes that many organic substances, including humic substances, retard the formation of $CaCO_3$ crystals by blocking spiral dislocation growth sites; this forces the crystals to grow by a much slower surface nucleation process.

Other investigators such as Otsuki and Wetzel (1973) have also shown that the presence of humic substances significantly retards the precipitation rate of $CaCO_3$. They note that of the waters compared those with the higher presence of carboxyls retarded the precipitation rate most. Stewart and Wentzel (1981) found that the inhibition of calcium carbonate precipitation by fulvic acid is marked even at low concentrations. The amount of $CaCO_3$ precipitated under laboratory conditions was inversely related to the amount of fulvic acid present and that beyond certain concentrations $CaCO_3$ precipitation was prevented completely. Tuson (1986), using experimental batch tests, showed that the $CaCO_3$ precipitation rate is reduced considerably (up to 3 orders of magnitude) when brown waters of the South African Western Cape are used.

From the above it can be seen that the presence of humic substances in brown water is likely to result in increased aggressive attack of cement concrete. First, the dissolution potential of a brown water is likely to be higher than its non humic substances containing counterpart due to the attainment of saturation being frustrated. Secondly, when saturation and supersaturation are eventually attained precipitation or formation of a protective $CaCO_3$ skin covering the more soluble $Ca(OH)_2$ is also frustrated. In the following section a brief survey of reported interactions between brown water and cement concrete is presented.

4.4 EFFECT OF BROWN HUMIC WATERS ON CEMENT CONCRETE

From the previous sections it can be expected that brown humic waters will be particularly aggressive to cement concrete by both taking up large quantities of calcium in calcium-humate complexes and retarding precipitation of $CaCO_3$ thus preventing the formation of a protective $CaCO_3$ skin. Unfortunately it would appear that there have been few experimental investigations into dissolution of cement concrete by waters containing humic compounds.

Halstead (1954) noted that "peaty moorland water", which drains from the Pennines, England, eroded concrete tunnels. He studied the ability of various mix designs and cement types to resist attack by these aggressive humic containing waters by immersing samples in a running stream. Over a four year period samples were tested against control cubes for compressive strength and loss of weight. Halstead found that all the types of concrete examined (*inter alia* OPC, Rapid hardening PC, low heat PC, sulphate resistant PC) behaved in a "remarkably similar" manner, all showed significant evidence of attack. The loss in strength to OPC over the period of four years is shown in Table 4.2. The proportional loss of strength was less with concrete of high strength. Concrete made of high alumina cement had a loss of strength of about two-thirds of that found to occur with ordinary mixes. An unbroken coat of bituminous paint was found to provide almost total immunity from attack. Gutt and Harrison (1977) note that all calcareous cements will be weakened by circulating acid constantly maintained at a high degree of acidity and that protection must be provided for concrete where acid effluents are continually flowing over the concrete. They note that such acidic conditions arise when organic acids such as the humic acids present in some natural waters flow over concrete.

TABLE 4.2 : Loss of strength of OPC concrete cubes exposed to soft water (from Halstead, 1954)

Duration of soft water immersion (years)	"Loss" of strength of concrete cubes made with Portland cement stored in running soft water (per cent)		
	Mean	Range	No. of results
0,5	14	3-27	24
1,0	22	16-32	20
1,5	38	35-40	4
3,5	51	48-54	2
4,0	45	32-53	18

Robertson and Rashid (1976), recognising that several investigations had already showed the strong solubilizing effect of humic substances on a number of metallic salts, rock forming minerals, clay minerals and silicates experimentally investigated the effect of humic substances on concrete. Unlike Halstead (1954) they did not expose the cement concrete to flow conditions but rather placed a 131 cm^3 block of cement concrete into a litre of solution containing 10 mg/ℓ humic acid. The solution was stirred gently every 24 hours. A distilled water control was used. The quantities of Ca^{2+} released from the concrete into both solutions were monitored over fifteen days. Although the quantity of Ca^{2+} released was slightly higher for the humic water (up to 5 mg/ℓ) and Robertson and Rashid note that the solubility of Ca^{2+} was increased, these differences do not seem to be dramatic and are certainly significantly less than those reported by Baker (1973) and Halstead (1954). Furthermore, Robertson and Rashid report the formation of an organic coating on the surface of the concrete which they claim appears to have a protective effect from further aggression.

Eglinton (1975), in reviewing the available literature, notes that the degree of attack by standing humic waters to mass concrete is negligible; he notes, however, that thin-walled structures such as field drains and culverts carrying peaty water showed significant evidence of attack. Eglinton further reports that the rate of aggression is essentially dependent on the solubility of the calcium salts formed by the organic acids. Where the characteristics of the humic substances are such that calcium salts are highly soluble the water is more aggressive. He further notes that physical conditions such as flow regime greatly affect the rate of aggression, i.e. where the formation of calcium salts on the cement concrete surface is frustrated aggression will be significant.

In conclusion, it can be expected that brown waters will be aggressive to cement concrete. Whether a brown water with acidity, calcium and pH values equal to those of a white water will be more or less aggressive is not clear in the literature.

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SECTION A

CHAPTER 5

EXPERIMENTAL INVESTIGATION INTO THE DISSOLUTION OF CEMENT CONCRETE MATERIALS BY AGGRESSIVE WATERS

5.1 INTRODUCTION

Chapter 1 introduces the concept that carbonation of OPC concrete may reduce the rate of attack by aggressive waters; it is hypothesized that this is as a result of the conversion of more soluble free lime ($Ca(OH)_2$) in the cement matrix to less soluble calcium carbonate ($CaCO_3$) during the carbonation process. This hypothesis needs to be tested by monitoring the dissolution of uncarbonated OPC and carbonated OPC exposed to aggressive water. Furthermore, as fly ash additives are presently a popular choice in cement concrete mix design where concrete faces harsh exposure conditions (Alexander, 1989), the dissolution of uncarbonated 30% fly ash OPC will also be monitored thereby providing a further comparative indicator.

Hence three cement concrete types are used in this investigation i.e. carbonated OPC, uncarbonated OPC and uncarbonated 30% fly ash OPC.

When considering the aggressive waters to be used to test the hypothesis a water which has already been identified as being of interest is brown humic water. Local brown waters are readily available for use, however as the role played by the humic substances present in such waters is not fully understood (see previous chapter), an aggressive water not containing humic substances should also be used. Two aggressive waters will therefore be used in this investigation, raw brown water and distilled water.

The principal objective of this investigation is thus to :

monitor and compare rates of dissolution of uncarbonated OPC concrete, carbonated OPC concrete and uncarbonated 30% fly ash OPC concrete exposed to aggressive "brown" water and aggressive "white" water.

5.2 MONITORING OF DISSOLUTION OF VARIOUS CEMENT TYPES

5.2.1 Introduction

Monitoring of aggressive attack by waters on cement concrete types can either be via measuring physical changes to the cement concrete sample with time (e.g. mass loss) or via measuring changes to the water's chemical characteristics with time (e.g. changes in pH, calcium and Alkalinity). Accurate measurement of physical changes to the concrete sample are difficult and require extended exposure periods before noticeable trends develop. In comparison changes to the chemical characteristics of water can be relatively easily monitored and are considerably more sensitive making this approach preferable when considering laboratory scale tests.

The ability to monitor reactions between a water and a cement concrete will not only be dependent on the aggressiveness of the water but also on parameters such as water volume to concrete surface area ratio and flow regime. For example, water quality changes to an aggressive water over a length of say one kilometre of cement type pipe are likely to be substantial and easily monitored. On the other hand water quality changes where large volumes of quiescent water are in contact with a small surface area of cement concrete are likely to be small and difficult to monitor. Unfortunately the use of extended pipe systems for each exposure condition considered in a laboratory study such as this is impractical. However a simulation is possible by immersing cement concrete samples into tanks containing stirred water. A set water volume to cement concrete surface area ratio is chosen. This approach makes use of exposure cycles where cycle duration is chosen to be such that significant changes in chemical characteristics of the water occur during a cycle. At the end of a cycle a new cycle is started by replacing the "old" water with fresh raw water and continuing as before.

This investigation makes use of cyclic exposure of three cement concrete types i.e. carbonated OPC, uncarbonated OPC and uncarbonated 30% fly ash OPC to two water types i.e. brown water and distilled water.

5.2.2 Experimental preparation

(a) Cement mix design and materials

Cement concrete test speciments were designed to give a 28 day compressive strength of 20 MPa. This is lower than normally would be used for exposure to aggressive waters and was chosen so as to both accelerate the dissolution process and exaggerate differences between the cement concrete types. To ensure good compaction a slump of 35 mm was used.

The mix design for the OPC concrete was 3,10 : 3,18 : 1,00 : 0,80 of washed gravel : sand : ordinary Portland cement : Water. An equivalent fly ash replacement mix was designed to give the same 28 day compressive strength and slump. The mix design was 4,43 : 4,64 : 0,43 : 1,00 : 1,06 of washed gravel : sand : fly ash : ordinary Portland cement : water. The aggregates used were local Cape Flats sand and Malmesbury shale coarse aggregate. The dune sand typically has very little fines content. The crushed coarse aggregate was 13 mm and flaky. The fly ash used is Lethabo Classified fly ash.

(b) Cement concrete sample preparation

When preparing a mix, cement, fly ash (where applicable), sand and dry aggregate were placed into a mechanical mixer. The mixer was started and the water slowly added. The freshly mixed concrete was cast into standard 100 mm cube steel moulds and cylindrical PVC moulds of the dimensions, diameter = 70,6 mm and height = 75 mm. (The former being used for 28 day compressive strength tests and the latter for dissolution tests).

To cast the concrete, the lightly oiled moulds were placed onto a vibrating table where the concrete was cast in three compacted layers. The exposed face of the sample was trowelled and the samples were left to set under wet hessian for 24 hours. After the initial 24 hour period the samples were placed in 20°C water baths for 28 days. At the end of this period six of the OPC cylindrical samples were carbonated to a depth of approximately 16 mm using the accelerated carbonation chamber (see Chapter 10, Section B). Six cylindrical samples of each of the uncarbonated OPC and 30% fly ash mixes were placed into an equivalent chamber with a high relative humidity (> 95%) and a normal atmospheric partial pressure of carbon dioxide ($\bar{p}CO_2 \sim 0{,}00035$ atmospheres) to prevent gaseous phase carbonation for the duration of the carbonation process. At the end of this period all of the cylindrical samples were exposed to dissolution experiments as discussed under experimental procedures, i.e. Section 5.2.3.

(c) Dissolution tanks

Dissolution tanks were constructed for each of the experimental combinations. These perspex tanks were of dimensions 490 x 490 x 680 mm (see Figure 5.1) and included a sampling port. The sampling port was used both for the taking of samples at set intervals and for the drainage and refilling of the tanks at the end of cycles.

A metal 'H' frame, made out of angle iron, fitted to the top of the tank supported the electric paddle stirrer which ran continuously. The concrete samples were suspended from the frame using nylon fishing line to hang in mid water. A polystyrene board, sized to snugly fit the tank, floated on the water surface minimizing uptake of carbon dioxide from the atmosphere. As each cement concrete sample cylinder was of the same dimensions and each tank was filled with the same volume of water a constant water volume to cement concrete surface area ratio exists for each exposure condition.

(d) Raw water

The two aggressive raw waters used for the dissolution experiments were brown humic water and distilled water. The brown humic water was obtained from Kloofnek water treatment works (Cape Town) once a week. (See Appendix C for typical results from an analysis of this water). The distilled water was manufactured in the laboratory.

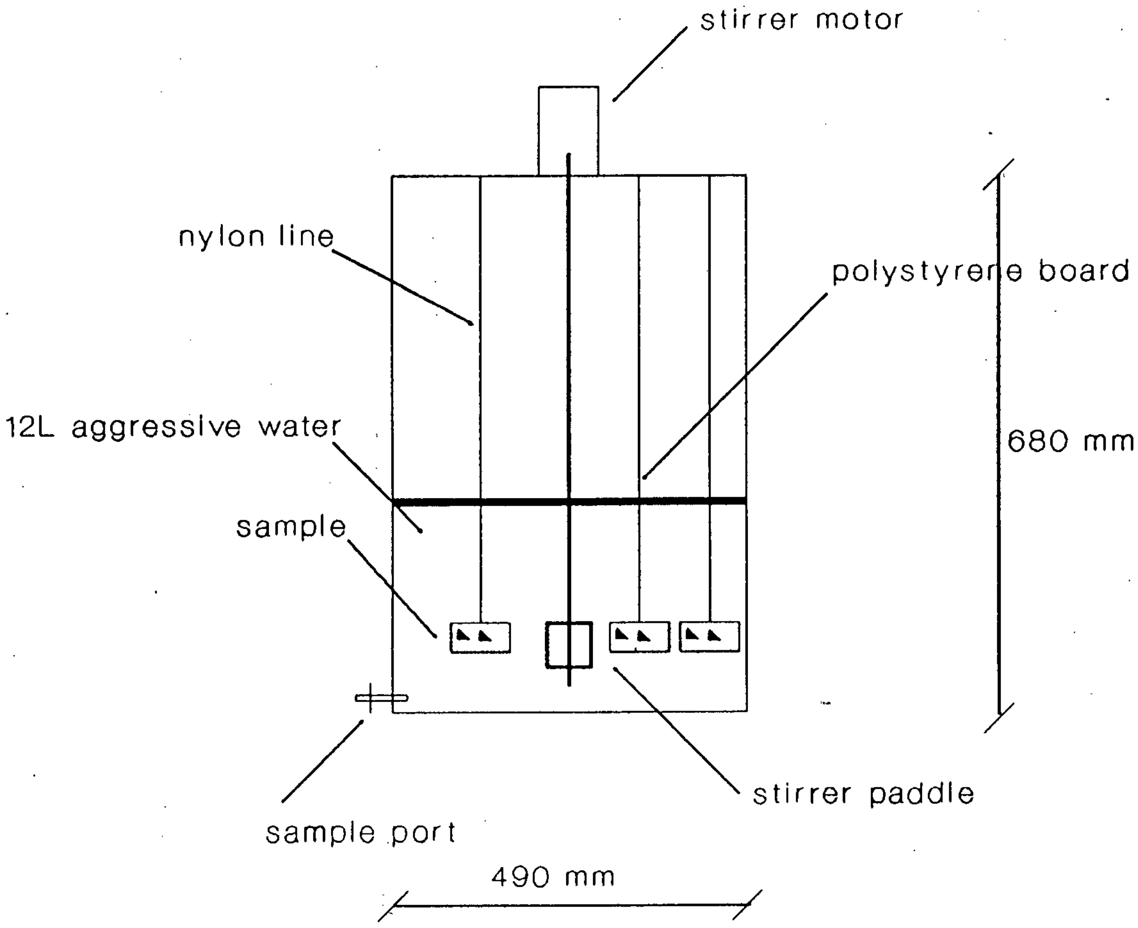


Figure 5.1 : Dissolution tank set up.

5.2.3 Experimental procedure

(a) Dissolution tests

Each of the three cement concrete types used was exposed to the two water types i.e. six dissolution tanks were used. In each tank three cement concrete cylinders of a particular cement concrete type were suspended independantly by nylon fishing line to hang in mid water. The tanks were filled via the sampling port with 12 litres of brown water or distilled water as necessary, giving a water volume to cement concrete surface ratio as follows :

$$\text{Surface area} = \{ (2 * \pi * r^2) + (2 * \pi * r * h) \} * 3$$
$$= 733{,}92 \text{ cm}^2$$
$$\text{Volume} = 12 \ \ell$$
$$= 12\ 000 \text{ cm}^3$$
$$\text{Volume/Surface area ratio} = \frac{12\ 000}{733{,}92}$$
$$= 16{,}35 \text{ cm}$$

The polystyrene board was adjusted to ensure that an air-water interface did not exist. The stirrer was then started marking the beginning of a cycle.

A sample of approximately 150 mℓ was collected in a sampling vessel at 24 hours, 48 hours and 72 hours. After the 72 hour sample had been obtained, i.e. the end of a three day cycle had been reached, the stirrer was switched off, the dissolution tank was drained, the walls were scrubbed and the tank was rinsed clean. The tank was immediately refilled with 12 ℓ of fresh water and the next cycle started.

(b) Water quality measurements

(i) pH Measurements :

The pH of the samples was measured using a calibrated Radiometer PHM 64 meter. Standard NBS buffer solutions were used to calibrate the meter and probe.

(ii) Alkalinity Measurements :

The $H_2CO_3^*$ alkalinity (Alkalinity) and HCO_3^- alkalinity (phenolphthalein alkalinity) of the samples were measured by titrating the samples with standard mineral acid to potentiometric endpoints as outlined in section 2.3.3. The endpoint for $H_2CO_3^*$ alkalinity was pH 5,0 and for HCO_3^* alkalinity pH 8,4.

This method of alkalinity measurement was checked initially by comparison with Gran titrations and found to be accurate.

(iii) Calcium measurements :

Calcium measurements were conducted on all of the samples using the EDTA titrimetric method as laid out in Standard Methods (1985).

To ensure that this method was accurate when considering the brown water where the humic substances would complex the calcium ions, test solutions containing known concentrations of calcium were made up.

The EDTA titrimetric method was shown to be accurate when dealing with the brown water of Kloofnek.

5.3 ANALYSIS OF TEST RESULTS

5.3.1 Introduction

In section 3.6 it was shown that when an aggressive water is in contact with cement concrete, dissolution of calcium minerals occurs resulting in changes to both the bulk water dissolved calcium concentration and alkalinity (due principally to lime and/or calcium carbonate dissolution). Dissolution can thus be monitored effectively either via measurement of changes in aqueous calcium concentrations or via measurement of changes to $H_2CO_3^*$ alkalinity and/or HCO_3^- alkalinity. (Measurement of all these parameters supplies a means of cross checking the accuracy of dissolution monitoring.)

In this investigation measurement of calcium, $H_2CO_3^*$ alkalinity, HCO_3^- alkalinity and pH was carried out at 24 hour intervals for each three day cycle throughout the investigation (see Appendix D). An analysis of these results provides a description of the interaction between the cement concretes and the various water types with time. Dissolution results are presented in terms of changes in aqueous calcium concentrations. $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity measurements are used to both confirm calcium dissolution results and to provide some indication as to the extent of carbon dioxide exchange between the gaseous and supposedly isolated aqueous phase during the three day cycle period.

It should be noted that such an experimental method only gives comparison of the <u>relative</u> abilities of the various cement materials to withstand aggression. The observation cannot be extrapolated to give expected in situ rates of aggressive attack. (This arises because during a three day cycle the quality of the water changes significantly from the raw water characteristics).

5.3.2 Experimental results

5.3.2.1 White water

Each of the three cement concrete types was exposed to aggressive white water (distilled water) for a duration of thirty-four three day cycles. Measurements of chemical water characteristics were taken at 24 hour intervals during the three-day cycles for the duration of the investigation. Figures 5.2 to 5.4 show the measured calcium concentrations for each of the cement concrete types on the first, second and third day of the three-day cycles respectively over 34 cycles. As the initial raw water calcium concentration is zero the calcium concentration measured on the third day gives the total calcium dissolution for a particular cycle, i.e. the rates presented are rates of calcium removal occurring over one, two or three days during a three-day cycle.

To provide a clearer illustration of the aggressive attack by white water one can consider the total cumulative mass of calcium removed with time from the cement concrete specimens. Firstly, the mass of calcium removed during a particular cycle is simply the dissolved calcium concentration at the end of a three-day cycle (in mg/ℓ) multiplied by the volume of water that the sample has been in contact with (in ℓ). Secondly the cumulative calcium removal is the sum of such removals. The cumulative calcium removal therefore gives the total mass of calcium removed from the cement concrete specimens with time during the investigation (see Figure 5.5).

5.3.2.2 Brown water

The three cement concrete types were subjected to dissolution tests in brown aggressive water as above for white water. Figures 5.6 to 5.8 show the monitored calcium dissolution rates for one-day, two-day and three-day cycles over 34 three-day cycles. (For these brown waters the initial rain water calcium concentration was about 4 mg/ℓ as $CaCO_3$, this was taken into account in determining dissolution data). Figure 5.9 shows cumulative calcium removal from the various cement concrete types for 34 three-day cycles.

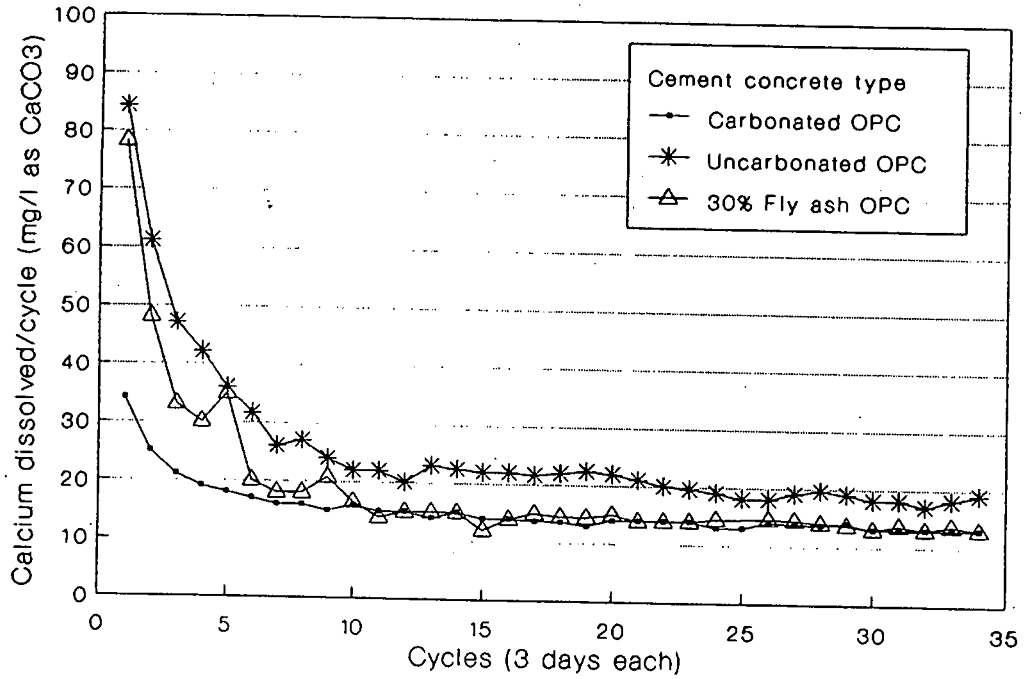


Figure 5.2 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by distilled water on day one of repeated three day exposure cycles.

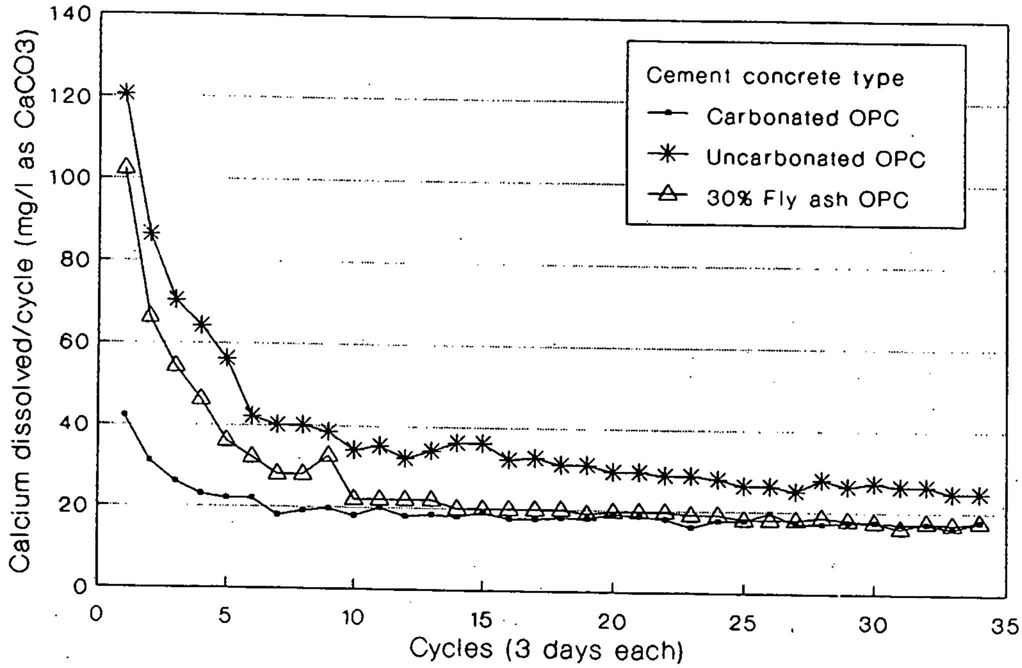


Figure 5.3 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by distilled

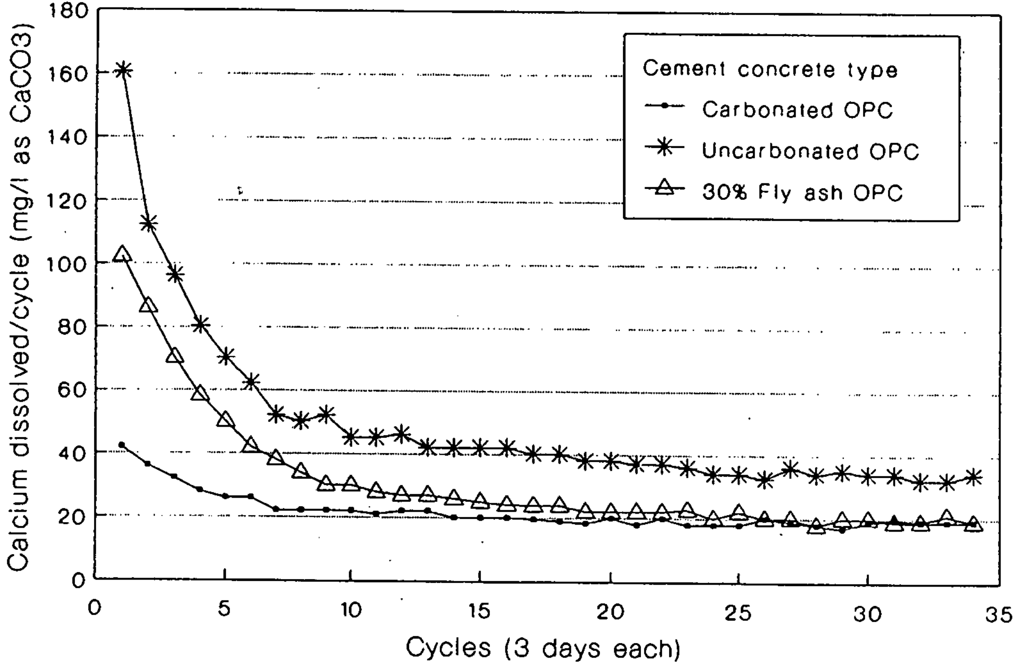
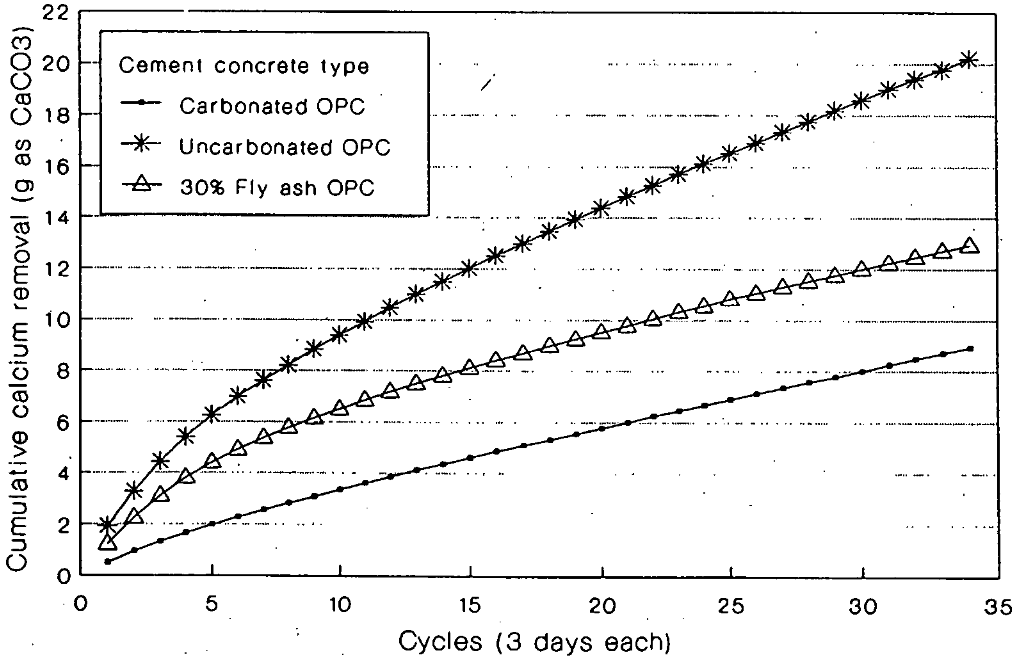


Figure 5.4 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by distilled water on day three of repeated three day exposure cycles.



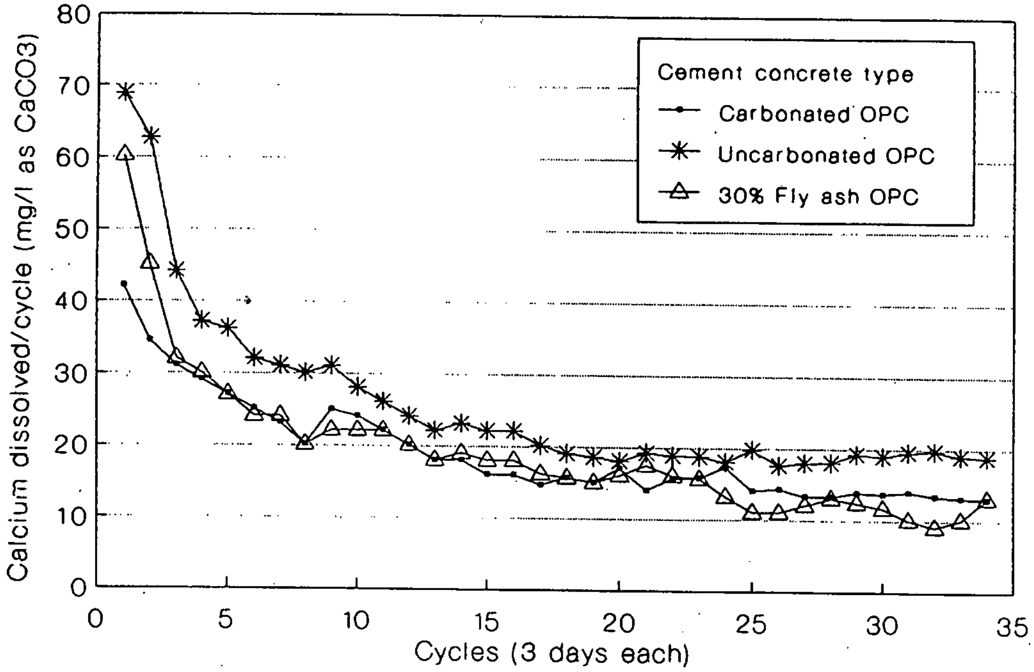


Figure 5.6 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by brown water on day one of repeated three day exposure cycles.

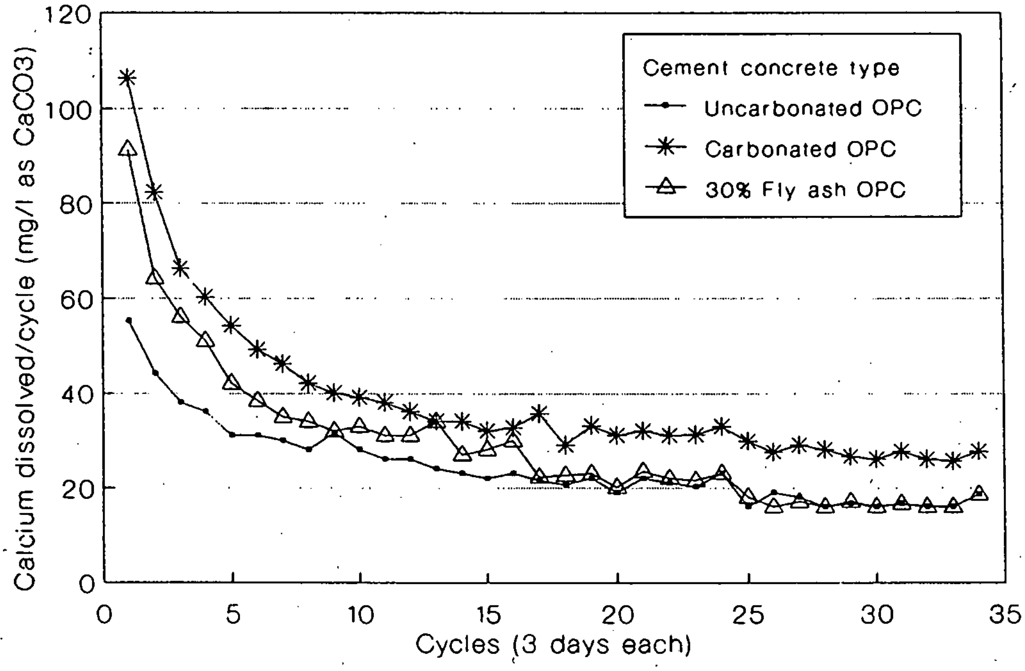


Figure 5.7 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by brown water on day two of repeated three day exposure cycles.

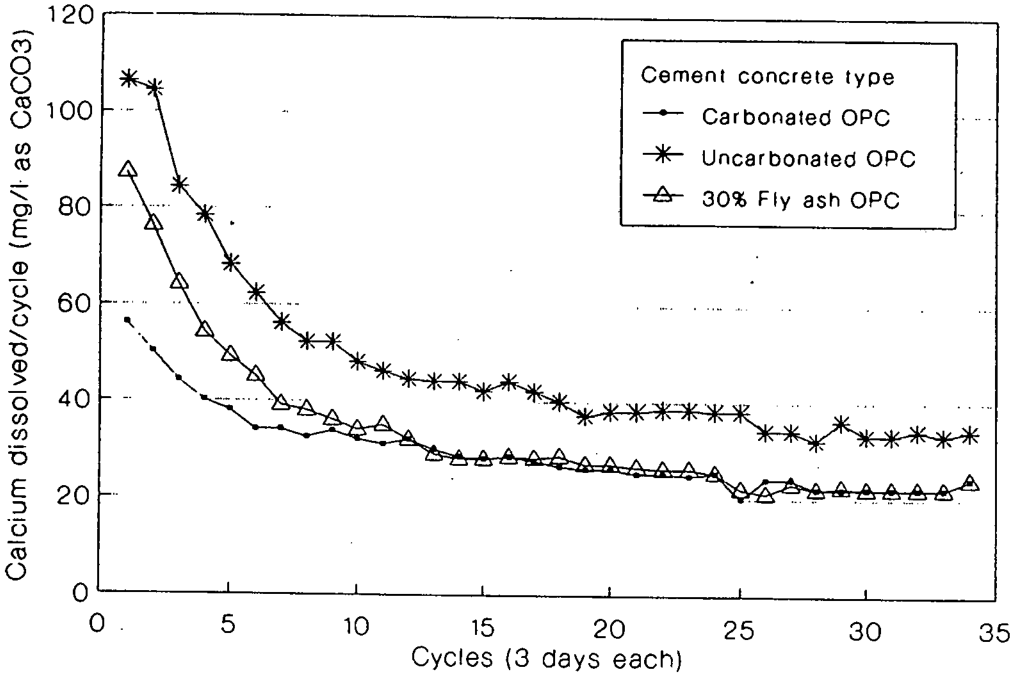


Figure 5.8 : Measured calcium dissolution of carbonated OPC, uncarbonated OPC and 30% fly ash OPC by brown water on day three of repeated three day exposure cycles.

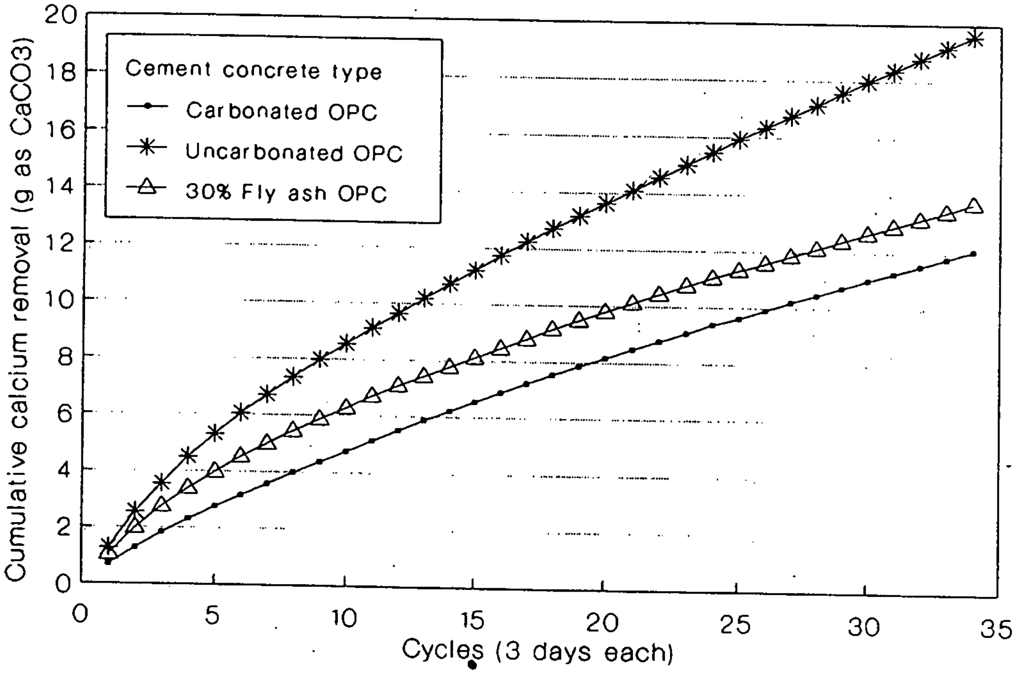


Figure 5.9 : Cummulative calcium removal from carbonated OPC, uncarbonated OPC and 30% fly ash OPC by three day

5.3.3 Analysis of results

5.3.3.1 White water

(a) Analysis of calcium dissolution trends

Analysis of Figures (5.2 to 5.4) shows that dissolution results on day one, day two and day three during a three-day cycle follow the same trend, i.e. dissolution of calcium with time is highest for uncarbonated OPC, less for 30% fly ash OPC and least for carbonated OPC irrespective of whether a one-, two- or three-day time period is considered. Furthermore, all three cement concrete types exhibit initial relatively high dissolution values per cycle which gradually reduce and eventually become constant at reduced levels. These trends are most accentuated where time periods of three days are considered; comparison and discussion of results will be based on the day three trends presented in Figures (5.4 and 5.5).

An examination of Figure 5.4 shows that throughout the investigation the uncarbonated OPC undergoes the highest calcium dissolution rates. For all of the cement concrete types investigated the dissolution rates are initially high and decrease exponentially to an approximately constant value in approximately 10 cycles (30 days).

Referring to Figure 5.4 :

(i) Comparing the calcium dissolution rates for uncarbonated OPC with 30% fly ash OPC it can be seen that these follow similar trends, almost running parallel to each other throughout the investigation. The uncarbonated OPC consistently experiences higher calcium dissolution per cycle. From the second cycle onwards the difference in calcium dissolution per cycle is approximately constant throughout (a difference of 20 mg/ℓ as $CaCO_3$ in cycle 5, and 15 mg/ℓ as $CaCO_3$ in cycle 34).

(ii) Comparing the calcium dissolution rates for uncarbonated OPC with carbonated OPC it can be seen that the uncarbonated OPC generally experiences higher calcium dissolution per cycle. Initially calcium dissolution per cycle for uncarbonated OPC is considerably higher than for carbonated OPC (cycles 1 to 10). However, after the first ten cycles, during which calcium dissolution per cycle for the uncarbonated OPC drops dramatically whilst calcium dissolution per cycle for carbonated OPC drops considerably less, an approximately constant difference in calcium dissolution per cycle occurs (23 mg/ℓ as $CaCO_3$ in cycle 10, and 15 mg/ℓ as $CaCO_3$ in cycle 34).

(iii) Comparing the calcium dissolution rates for carbonated OPC with 30% fly ash OPC it can be seen that although the latter initially experiences considerably higher calcium dissolution rates (cycles 1 to 5) these differences decrease rapidly. After ten cycles the difference is relatively small (± 8 mg/ℓ as $CaCO_3$) and continues to decrease gradually until cycle 27 whereafter the calcium dissolution rates are very similar for these two cement types.

Referring to Figure 5.5 :

(i) Comparing the cumulative dissolution of calcium from uncarbonated OPC with that from 30% fly ash OPC shows that although the initial rate of cumulative dissolution is similar (up to cycle 4), thereafter that of the 30% fly ash OPC decreases significantly relative to the uncarbonated OPC.

(ii) Comparing the cumulative dissolution of calcium from uncarbonated OPC with that from carbonated OPC confirms that the carbonated OPC undergoes considerably lower levels of aggressive attack. The carbonated OPC shows an almost constant rate of accumulative calcium dissolution (as depicted by the flat shape in Figure 5.5).

(iii) Comparing the cumulative dissolution of calcium from carbonated OPC with 30% fly ash OPC shows that initially the 30% fly ash OPC undergoes higher rates of cumulative calcium dissolution (cycles 1 to 5). Thereafter the cumulative calcium dissolution rate for 30% fly ash OPC decreases until equal to that of the carbonated OPC.

(b) <u>Comparison of alkalinity and calcium measurements</u>

In section 5.3.1 it was noted that in addition to measurement of dissolved calcium concentration, measurement of both $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity were taken throughout the duration of the investigation. It was also noted that these alkalinity measurements can be used to both (i) confirm dissolved calcium measurements, and (ii) provide an indication of the extent to which carbon dioxide exchange between the gaseous and aqueous phase occurs in a particular cycle. In this section the $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity results will be analysed in such a manner as to provide the above information.

(i) Confirmation of calcium measurements via analysis of changes in $H_2CO_3^*$ alkalinity

In section 3.5 it was shown that when cement concrete is in contact with an aggressive water (i.e. a water undersaturated with $CaCO_3$ the following changes occur: Firstly, if the cement concrete surface is uncarbonated the dissolution of free lime occurs as described by Equation (3.15), i.e.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Secondly, if the cement concrete surface is carbonated dissolution of calcium carbonate occurs as described by Equation (3.16), i.e.

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

The effects of these changes on $H_2CO_3^*$ alkalinity can be determined from Equation (2.30), i.e.

$$\Delta H_2CO_3^* \text{ alkalinity} = CO_3^{2-} \text{ (added} + HCO_3^- \text{ (added)} + OH^- \text{ (added)} \\ - H^+ \text{ (added)}$$

(where the use of no brackets indicate that species concentrations are expressed in mg/ℓ as $CaCO_3$).

Thus for lime, i.e. $Ca(OH)_2$, dissolution

$$\Delta H_2CO_3^* \text{ alkalinity} = \Delta OH^- = Ca(OH)_2 \text{ dissolved} \\ = \Delta Ca \qquad (5.1)$$

and for calcium carbonate, i.e. $CaCO_3$, dissolution

$$\Delta H_2CO_3^* \text{ alkalinity} = \Delta CO_3^{2-} = CaCO_3 \text{ dissolved} \\ = \Delta Ca \qquad (5.2)$$

Equations (5.1 and 5.2) show that irrespective of whether lime (uncarbonated cement concrete) or calcium carbonate (carbonated cement concrete) dissolve, the same changes occur in both $H_2CO_3^*$ alkalinity and calcium concentrations (when both are expressed in mg/ℓ as $CaCO_3$). Consequently, the changes in $H_2CO_3^*$ alkalinity per cycle should be the same as the measured change in calcium concentration per cycle presented earlier. The expected close agreement between changes in $H_2CO_3^*$ alkalinity and calcium were indeed found to occur.

In Figures 5.10 a, b and c are shown plotted the changes in $H_2CO_3^*$ alkalinity and calcium concentration per cycle for the three cement concrete types exposed to aggressive white water.

Inspection of Figures 5.10 a, b and c show that usually there is close agreement between the $H_2CO_3^*$ alkalinity measurements and the calcium measurements for all three cement concrete types. The exception being the first four cycles of the carbonated OPC where the changes in calcium per cycle are about 20% higher than changes in $H_2CO_3^*$ alkalinity. For this isolated case, it is not possible to explain these observed differences or to state which of the two is the more accurate.

(ii) Calculation of carbon dioxide uptake via analysis of changes in HCO_3^- alkalinity

In Chapter 2, HCO_3^- alkalinity was defined in Equation (2.24) as

$$HCO_3^- \text{ alkalinity} = CO_3^{2-}/2 + OH^- - H^+ - H_2CO_3^*/2$$

(where the use of no brackets indicate that species concentrations are expressed in mg/ℓ as $CaCO_3$).

When dissolution of uncarbonated cement concrete and carbonated cement concrete occurs as described earlier by Equations (3.15 and 3.16) respectively the stoichimetric changes to HCO_3^- alkalinity on the $CaCO_3$ scale, are as follows :

$$\begin{aligned}\Delta HCO_3^- \text{ alkalinity} &= CO_3^{2-}/2 = CaCO_3 \text{ dissolved}/2 \\ &= \Delta Ca/2 \qquad (5.4)\end{aligned}$$

In Tables 5.1 a, b and c are listed *inter alia* measured changes in calcium and HCO_3^- alkalinity for the three cement concrete types exposed to white water. Referring to Tables 5.1 (a) and (b), for the dissolution of uncarbonated OPC and 30% fly ash OPC, it is immediately apparent that the relationship between HCO_3^- alkalinity changes and calcium changes for uncarbonated cement concrete as described by Equation (5.3) is not satisfied, i.e. the HCO_3^- alkalinity change is consistently significantly

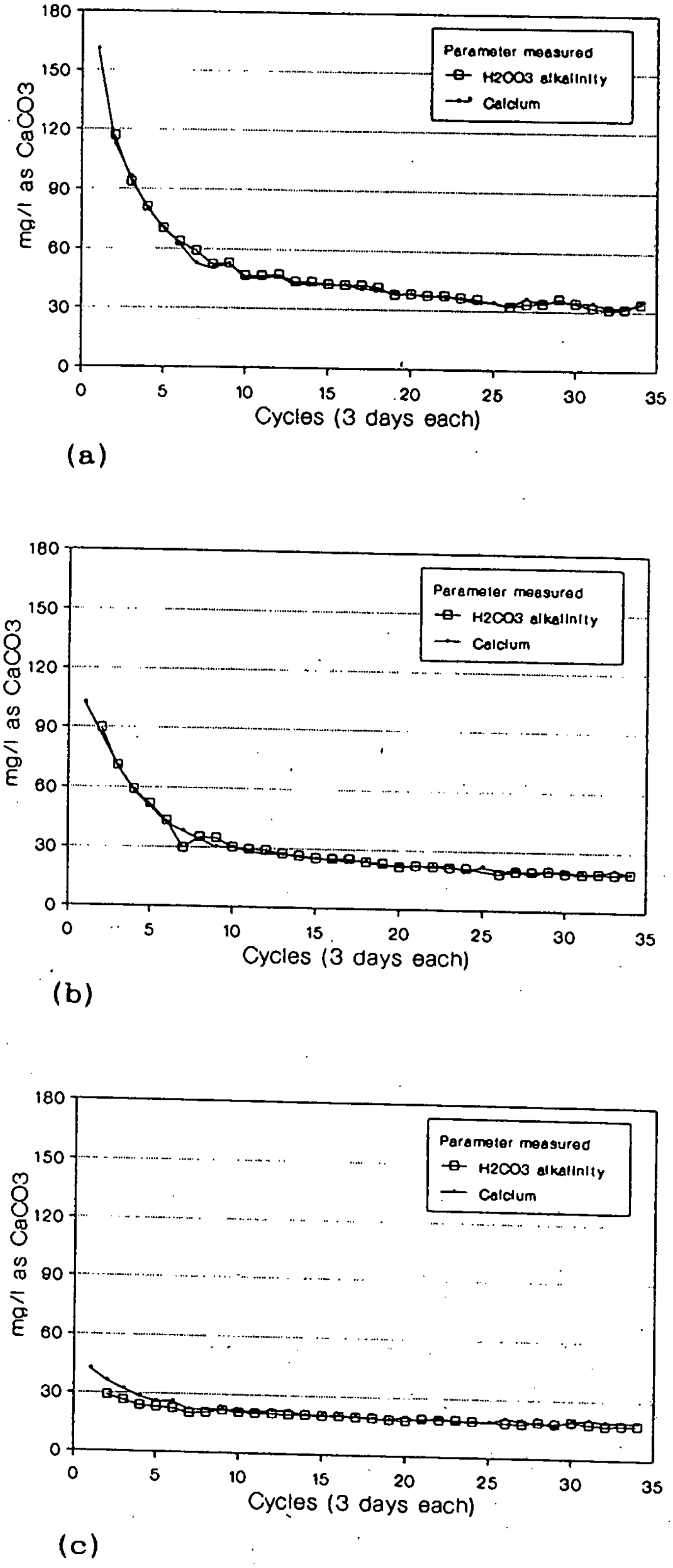


Figure 5.10 (a, b & c) : Measured calcium and $H_2CO_3^*$ alkalinity values on day three of repeated three day distilled water exposure

less than the change in dissolved calcium concentration. Referring to Table 5.1(c), for the dissolution of carbonated OPC, shows that again the expected relationship between HCO_3^- alkalinity and calcium, as described by Equation (5.4), is not satisfied; HCO_3^- alkalinity values are again lower than expected.

The reason for the discrepancies between changes in calcium concentration and changes in HCO_3^- alkalinity per cycle noted above can only be explained by the concomitant uptake of carbon dioxide from air during a three-day cycle. Referring to Equation (2.24) uptake of carbon dioxide by the water body causes stoichiometric decrease in HCO_3^- alkalinity (without changing either calcium concentration or $H_2CO_3^*$ alkalinity). It is apparent therefore that it is posible to quantify carbon dioxide uptake per cycle as follows :

For uncarbonated cement concrete (i.e. uncarbonated OPC amd 30% fly ash OPC from Equations (2.24 and 5.3)

$$\begin{aligned} \Delta CO_2 &= \Delta H_2CO_3^* \\ &= \Delta CO_3^{2-} + 2.\Delta OH^- - 2.\Delta H^+ - 2.\Delta HCO_3^- \text{ alkalinity} \\ &= \Delta Ca - 2.\Delta HCO_3^- \text{ alkalinity} \end{aligned} \qquad (5.6)$$

The calculated values for carbon dioxide uptake are listed in column 6 of Tables 5.1 a, b and c respectively.

For uncarbonated OPC the carbon dioxide uptake per cycle varied between 28 mg/ℓ as $CaCO_3$ (Cycle 2) and 24 mg/ℓ as $CaCO_3$ (Cycle 24), with an average of about 27 mg/ℓ a $CaCO_3$. Closely similar carbon dioxide uptake occurred during the 30% fly ash OPC dissolution cycles with an average value of about 25 mg/ℓ a $CaCO_3$ per cycle. For the uncarbonated OPC the average carbon dioxide uptake is significantly less than for the uncarbonated cement concretes with an average value of about 14 mg/ℓ as $CaCO_3$. The higher carbon dioxide uptake in the case of lime

TABLE 5.1 (b) : pH, calcium, HCO_3^- alkalinity, $H_2CO_3^*$ alkalinity, CO_2 uptake and CO_3^{2-} acidity for 30% fly ash OPC on day three for exposure cycles to distilled water.
(all concentrations mg/ℓ as $CaCO_3$)

Cycle	pH	Calcium	HCO_3^- alk	$H_2CO_3^*$ alk	CO_2 uptake	CO_3^{2-} acid
1		102				
2	11,50	86	75	90	23	-156
3	11,24	70	56	71	28	-113
4	11,19	58	46	59	24	-93
5	10,94	50	35	52	30	-74
6	10,98	42	31	43	22	-65
7	10,65	38	19	30	39	-20
8	10,63	34	23	35	22	-48
9	10,51	30	21	35	19	-50
10	10,44	30	17	30	27	-34
11	10,63	28	17	29	22	-36
12	10,53	27	17	29	21	-37
13	10,67	27	15	27	24	-30
14	10,30	26	13	26	26	-27
15	10,53	25	13	25	24	-26
16	10,11	24	10	25	28	-21
17	10,38	24	12	25	25	-25
18	10,15	24	10	24	28	-20
19	10,38	22	11	23	23	-23
20	10,20	22	10	21	24	-19
21	10,35	22	10	22	25	-20
22	10,13	22	9	22	26	-18
23	10,32	23	10	21	25	-17
24	10,14	20	9	21	22	-20
25		22				
26	10,06	20	7	19	26	-11
27	10,17	20	8	20	24	-15
28	10,06	18	8	20	21	-19
29	10,18	20	10	20	21	-19
30	9,93	20	7	19	26	-12
31	10,13	19	6	19	25	-12
32	9,98	19	7	19	25	-14

TABLE 5.1 (c) : pH, calcium, HCO_3^- alkalinity, $H_2CO_3^*$ alkalinity, CO_2 uptake and CO_3^{2-} acidity for carbonated OPC on day three for exposure cycles to distilled water.
(all concentrations mg/ℓ as $CaCO_3$)

Cycle	pH	Calcium	HCO_3^- alk	$H_2CO_3^*$ alk	CO_2 uptake	CO_3^{2-} acid
1		42	8	29	26	26
2	9,73	36	8	29	20	20
3	9,70	32	7	26	17	17
4	9,67	28	5	24	17	17
5	9,60	26	5	23	16	16
6	9,77	26	6	22	15	15
7	9,56	22	4	20	13	13
8	9,48	22	4	21	13	13
9	9,57	22	4	22	13	13
10	9,39	22	4	21	15	15
11	9,65	21	4	21	14	14
12	9,52	22	3	21	16	16
13	9,71	22	4	20	15	15
14	9,43	20	3	20	15	15
15	9,70	20	3	20	13	13
16	9,51	20	3	20	13	13
17	9,53	20	3	20	14	14
18	9,46	19	3	19	12	12
19	9,62	18	4	18	11	11
20	9,51	20	3	18	14	14
21	9,58	18	3	19	12	12
22	9,47	20	3	19	14	14
23	9,57	18	3	19	12	12
24	9,44	18	3	19	12	12
25		18				
26	9,35	20	3	18	15	15
27	9,50	19	3	17	13	13
28	9,45	18	3	18	13	13
29	9,63	17	3	18	11	11
30	9,33	19	2	19	15	15
31	9,49	20	2	18	16	16

5.3.3.2 Brown water

(a) Analysis of calcium dissolution trends

An analysis of Figures (5.6 to 5.8) confirms the observations made on the white water dissolution results, i.e. (i) dissolution results in terms of day one, day two and day three of the three-day cycles follow a general trend in which dissolution of calcium with time is highest for uncarbonated OPC, less for 30% fly ash OPC and least for carbonated OPC, and (ii) all three cement concrete types exhibit initially high dissolution values per cycle which decrease exponentially becoming approximately constant at reduced levels in later cycles.

An examination of Figure 5.8 shows that throughout the investigation the uncarbonated OPC undergoes the highest calcium dissolution rates. For all the cement concrete types investigated the dissolution rates are initially high decreasing exponentially over the first approximately 12 cycles (36 days). Thereafter the dissolution rates decrease gradually until cycle 25 (75 days) after which an approximately constant dissolution rate is maintained.

Referring to Figure 5.8 :

(i) Comparing the calcium dissolution rates for uncarbonated OPC with those of 30% fly ash OPC it can be seen that these follow similar trends throughout the investigation. The uncarbonated OPC consistently experiences higher dissolution rates. The magnitude of this difference varying slightly between cycle 3 (20 mg/ℓ as $CaCO_3$) and cycle 16 (15,6 mg/ℓ as $CaCO_3$) whereafter an almost constant difference of about 12 mg/ℓ as $CaCO_3$ exists.

(ii) Comparing the dissolution rates for uncarbonated OPC with carbonated OPC it can be seen that the uncarbonated OPC generally experiences higher calcium dissolution per cycle. Initially calcium dissolution per cycle for uncarbonated OPC is considerably higher than for carbonated OPC (cycles 1 to 6). Thereafter, as a result of the significant drop in calcium dissolution per cycle for uncarbonated OPC, the difference in calcium dissolution per cycle is considerably reduced. (In cycle 1, uncarbonated OPC dissolves 50 mg/ℓ as $CaCO_3$ more than carbonated OPC whilst in cycle 7 it only dissolves 22 mg/ℓ as $CaCO_3$ more). From cycle 10 onwards an approximately constant difference in calcium dissolution per cycle occurs (16 mg/ℓ as $CaCO_3$ in cycle 10, and 10 mg/ℓ as $CaCO_3$ in cycle 34).

(iii) Comparing the calcium dissolution rates for carbonated OPC with 30% fly ash OPC it can be seen that although the latter initially experiences significantly higher dissolution rates (31 mg/ℓ as $CaCO_3$ more in cycle 1) these differences decrease dramatically in the first five cycles (11 mg/ℓ as $CaCO_3$ more in cycle 5) decreasing further until from cycle 12 onwards there is no distinguishable difference between the calcium dissolution per cycle by brown water from 30% fly ash oPC and from carbonated OPC.

An examination of Figure 5.9, which shows cumulative calcium dissolution from the three cement concrete types by brown water, reinforces the observation that uncarbonated OPC is least resistant to aggressive attack.

Referring to Figure 5.9 :

(i) Comparing the cumulative dissolution of calcium from uncarbonated OPC with that from the 30% fly ash OPC shows that cumulative calcium dissolution is only similar in the first three cycles (as depicted by the slope of the plots). Thereafter cumulative calcium removal from 30% fly ash OPC decreases significantly relative to cumulative calcium removal from uncarbonated OPC.

(ii) Comparing the cumulative dissolution of calcium from uncarbonated OPC with that from carbonated OPC results in a very similar overall observation to that in (i) above. A noticeable difference, however, is that cumulative calcium dissolution is not similar in early cycles, i.e. the cumulative calcium removal rate (as depicted by the slope of the plots) is considerably less for carbonated OPC relative to the uncarbonated OPC throughout the investigation.

(iii) Comparing the cumulative dissolution of calcium from carbonated OPC with that from 30% fly ash OPC, the 30% fly ash OPC undergoes higher rates of cumulative calcium dissolution in early cycles (say, cycles 1 to 5). Thereafter the cumulative calcium dissolution rate for 30% fly ash is closely equal to that of the carbonated OPC.

(b) Comparisons of alkalinity and calcium measurements

In section 5.3.3.1 (b) it was shown that for white water relationships exist between changes in $H_2CO_3^*$ alkalinity, and HCO_3^- alkalinity and dissolved calcium per cycle. These relationships were shown to provide a means of cross-checking calcium mineral dissolution per cycle and assessing carbon dioxide uptake by the water body per cycle. This was possible because the initial and 'post three-day cycle' characteristics of the water body could be measured.

When considering the brown water the same analysis is possible for the calcium change per cycle. However, the changes in alkalinities are complicated by the presence of humic and fulvic acids - the alkalinity of these waters cannot be measured because the weak acid characteristics of the organic acids are unknown. Nevertheless some initial assessment is possible if we accept the humic and fulvic acid dissociation constants occur well below the pH obtained during dissolution tests. In which event we regard the organic acids simply as strong acids so that a titration of the raw brown water to pH 7,0 (a pH well above humic acid pH value) gives a measure of the initial acidity, i.e. negative alkalinity of the raw water. Such measurement for these waters gives initial $H_2CO_3^*$ alkalinity (and HCO_3^- alkalinity) equal to about -9 mg/ℓ as $CaCO_3$. Using the assumption that the initial $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity arise from the organic acids as outlined above, assessment of the reliability of calcium dissolution and carbon dioxide uptake per cycle is carried out in a similar fashion to that previously for white water.

(i) **Confirmation of calcium measurements via analysis of changes in $H_2CO_3^*$ alkalinity**

Making allowance for the initial negative $H_2CO_3^*$ alkalinity of the brown water, Equations (5.1 and 5.1) can be used to assess the accuracy of measured changes in calcium concentration per cycle as presented in Figure 5.8. Changes in $H_2CO_3^*$ alkalinity and calcium concentrations per three-day cycle for the three cement concrete types are plotted in Figures 5.11 a, b and c. Inspection of these figures shows that usually there is <u>close agreement between $H_2CO_3^*$ alkalinity measurements and the calcium measurements for all three cement concrete types</u>. This confirms earlier tests which indicated that calcium measurement by the EDTA titrametric method is accurate in brown water. It should be noted that, again, as for the white water dissolution tests, the first four cycles of the carbonated OPC are about 20 per cent higher than concomitant changes in $H_2CO_3^*$ alkalinity. Again, it is not possible to state which of the two parameters is the more accurate.

(ii) **Calculation of carbon dioxide uptake via analysis if change in HCO_3^- alkalinity**

Analysis of changes in HCO_3^- alkalinity with dissolution of cement concretes exposed to brown water shows that, as with white water, the expected relationships from dissolution of calcium carbonate and/or lime alone (i.e. Equations 5.3 and 5.4) are not satisfied. These discrepancies result from carbon

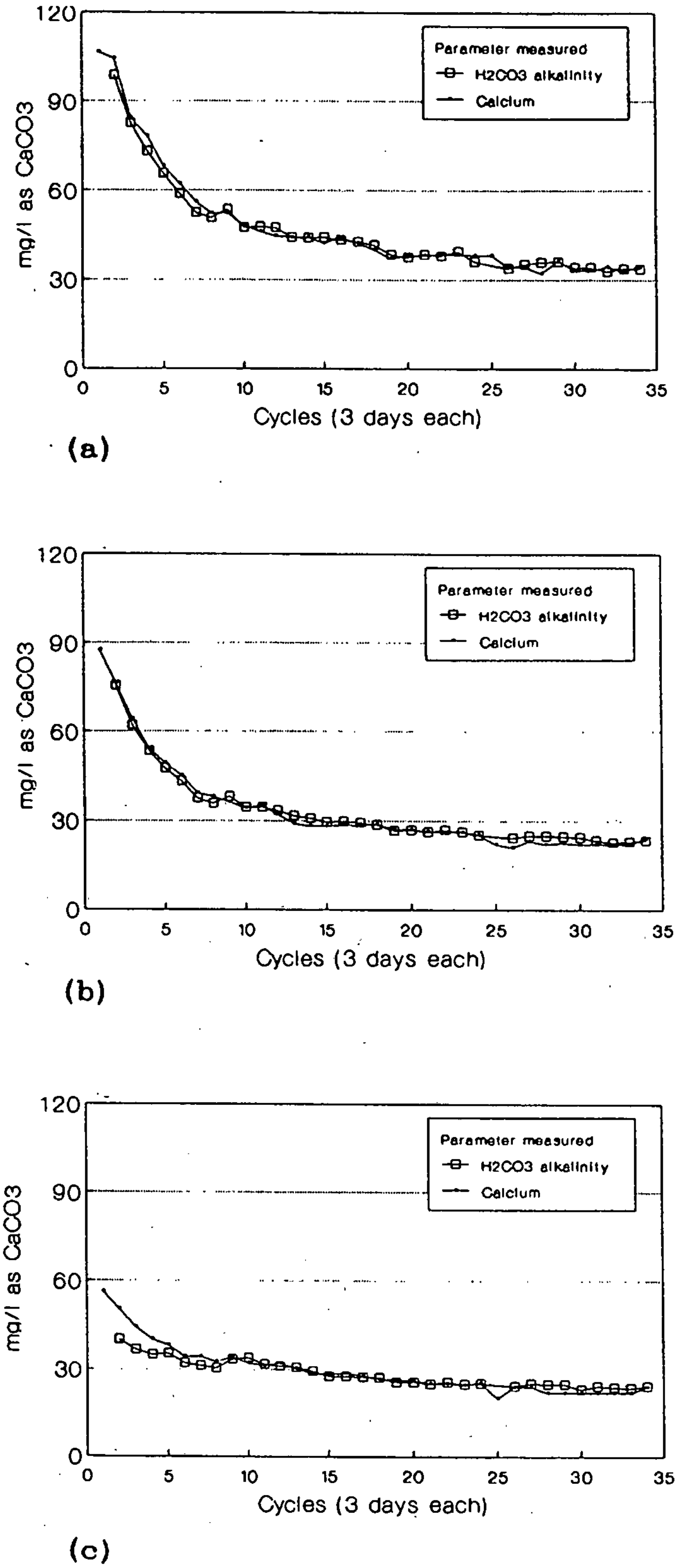


Figure 5.11 (a, b & c) : Measured calcium and $H_2CO_3^*$ alkalinity values on day

dioxide uptake during a particular cycle; the magnitude of carbon dioxide uptake can be determined via Equations (5.5 and 5.6) and is listed in column six of Tables 5.2 a, b and c. Comparison of carbon dioxide uptake per cycle by brown water can be seen to be similar to those by white water.

For uncarbonated OPC the average carbon dioxide uptake was about 35 mg/ℓ as $CaCO_3$ whilst for 30% fly ash OPC the average carbon dioxide uptake was similar, being about 31 mg/ℓ as $CaCO_3$; for the carbonated OPC the average carbon dioxide uptake was significantly lower with an average value of about 10 mg/ℓ as $CaCO_3$. As for white water the carbon dioxide uptake appears to be significantly higher for the uncarbonated cement concretes than for the carbonated cement concrete.

TABLE 5.2 (a) : pH, calcium, HCO_3^- alkalinity, $H_2CO_3^*$ alkalinity, CO_2 uptake and CO_3^{2-} acidity for uncarbonated OPC on day three for exposure cycles to brown water.
(all concentrations mg/ℓ as $CaCO_3$)

Cycle	pH	Calcium	HCO_3^- alk	$H_2CO_3^*$ alk	CO_2 uptake	CO_3^{2-} acid
1		106				
2	11,45	104	76	99	45	-53
3	11,18	84	62	83	40	-42
4	11,11	78	52	73	41	-32
5	10,93	68	45	66	41	-25
6	11,01	62	42	59	34	-25
7	10,70	56	34	52	38	-15
8	10,54	90	32	51	38	-12
9	10,51	52	31	54	46	-8
10	10,33	48	28	47	40	-8
11	10,39	46	25	48	45	-2
12	10,42	45	27	48	42	-6
13	10,51	44	25	44	39	-5
14	10,23	44	24	44	40	-4
15	10,46	42	24	44	39	-5
16	10,24	44	24	43	39	-5
17	10,36	42	24	43	38	-5
18	10,23	40	23	42	36	-5
19	10,34	37	21	38	35	-4
20	10,19	38	21	37	33	-4
21	10,34	38	21	38	35	-4
22	10,09	39	20	38	35	-3
23	10,24	39	21	40	36	-3
24	10,10	38	19	36	34	-2
25		38			0	
26	10,00	34	18	34	32	-2
27	10,02	34	17	35	36	1
28	10,03	32	18	36	36	-0
29	10,24	36	20	36	32	-4
30	10,05	33	18	34	32	-2
31	10,10	33	19	34	29	-5

TABLE 5.2 (b) : pH, calcium, HCO_3^- alkalinity, $H_2CO_3^*$ alkalinity, CO_2 uptake and CO_3^{2-} acidity for 30% fly ash OPC on day three for exposure cycles to brown water.
(all concentrations mg/ℓ as $CaCO_3$)

Cycle	pH	Calcium	HCO_3^- alk	$H_2CO_3^*$ alk	CO_2 uptake	CO_3^{2-} acid
1		87				
2	11,18	76	53	75	46	-105
3	11,18	64	42	62	45	-79
4	10,74	54	33	53	42	-65
5	10,55	49	29	47	41	-54
6	10,58	45	25	43	40	-47
7	10,18	39	20	38	39	-36
8	9,92	38	18	36	41	-30
9	9,85	46	17	38	58	-18
10	9,57	34	14	34	41	-28
11	9,77	35	14	35	42	-27
12	9,55	32	13	33	39	-28
13	9,59	29	12	32	34	-29
14	9,41	28	12	31	32	-29
15	9,49	28	12	29	32	-27
16	9,27	29	11	30	34	-25
17	9,37	28	11	29	34	-25
18	9,27	29	11	29	35	-22
19	9,36	27	11	27	31	-22
20	9,14	27	11	27	33	-21
21	9,22	27	11	26	32	-20
22	9,01	26	11	27	31	-23
23	9,20	26	11	26	31	-21
24	8,75	25	10	25	32	-19
25		22				
26	8,81	21	10	24	23	-26
27	8,41	23	9	25	28	-22
28	8,58	22	9	25	26	-24
29	9,00	23	10	25	25	-25
30	8,48	22	10	24	25	-24
31	8,75	22	10	23	25	-22

TABLE 5.2 (c) : pH, calcium, HCO_3^- alkalinity, $H_2CO_3^*$ alkalinity, CO_2 uptake and CO_3^{2-} acidity for carbonated OPC on day three for exposure cycles to brown water.
(all concentrations mg/ℓ as $CaCO_3$)

Cycle	pH	Calcium	HCO_3^- alk	$H_2CO_3^*$ alk	CO_2 uptake	CO_3^{2-} acid
1		56				0
2	9,22	50	12,84	40,21	25	25
3	9,15	44	12,84	36,71	19	19
4	9,07	40	11,00	34,87	18	18
5	8,97	38	12,09	35,29	14	14
6	9,03	34	10,50	32,03	13	13
7	8,64	34	10,00	31,20	14	14
8	8,33	33	8,53	30,25	15	15
9	8,65	30	9,86	33,34	10	10
10	8,28	32	10,25	33,79	12	12
11	8,50	31	9,71	31,66	12	12
12	8,35	32	9,00	30,95	14	14
13	8,42	30	9,00	30,59	12	12
14	8,05	29	8,71	29,16	11	11
15	8,03	28	8,20	27,45	12	12
16	7,95	29	8,20	27,62	12	12
17	7,97	28	8,20	27,28	11	11
18	7,98	27	8,20	27,10	10	10
19	8,11	26	8,20	25,56	10	10
20	7,93	26	8,20	25,56	10	10
21	7,83	25	8,37	24,88	8	8
22	7,89	25	8,20	25,56	9	9
23	7,91	25	8,20	24,88	8	8
24	7,73	25	7,68	25,22	10	10
25		20				
26	7,70	24	8,20	24,36	8	8
27	7,74	24	8,37	25,05	7	7
28	7,62	22	8,20	24,88	6	6
29	7,92	22	8,20	24,88	6	6
30	7,71	22	7,68	23,16	7	7
31	7,95	22	8,03	24,19	6	6

5.3.4 Discussion

The analysis of experimental results presented in Section 5.3.3 above, shows that the rate of calcium mineral dissolution differs between the three cement concrete types investigated. The general trend in these rates with time is similar irrespective of whether the aggressive water is "white" or "brown". The observed trends are as follows :

(a) Once steady dissolution rates were obtained, 30% fly ash OPC and carbonated OPC underwent closely the same calcium dissolution per three day cycle. The time required to attain steady state dissolution rates varied for the two water types, being approximately twice as long for the white water as compared with the brown water, i.e. 20 and 10 cycles respectively.

(b) Uncarbonated OPC experiences significantly higher dissolution rates than both 30% fly ash OPC and carbonated OPC. Once steady rates were obtained the uncarbonated OPC calcium mineral dissolution per three day cycle was 70% higher than those for 30% fly ash OPC and carbonated OPC in white water, and 55% higher in brown water.

The observed higher dissolution rate for uncarbonated OPC as compared to both carbonated OPC and 30% fly ash OPC are to be expected. In Chapter 3 it was shown that uncarbonated lime (i.e. $Ca(OH)_2$) is considerably more soluble than calcium carbonate (i.e. $CaCO_3$) and hence high dissolution rates for the former (i.e. uncarbonated OPC) can be expected. With regard to fly ash, the observed greater rate of dissolution for unbcarbonated OPC is also to be expected because fly ash is a natural pozzolon which reacts with free lime to form relatively insoluble silicate complexes, thereby reducing the mass of free lime available for dissolution.

A criticism of the investigation method is that significant gaseous CO_2 uptake by the aqueous phase occurred despite the precautionary measures adopted (see Section 5.2.2). Two effects of CO_2 uptake are to be expected :

(a) For both lime and calcium carbonate the dissolution potential will be increased, and

(b) where dissolution of lime occurs (i.e. the uncarbonated OPC and the 30% fly ash OPC), an unknown degree of calcium carbonate precipitation may occur from the aqueous phase resulting in an underestimation of calcium mineral dissolution per cycle.

With regard to (a) above, it was shown in Chapter 3 that the concomitant increase in Acidity associated with carbon dioxide uptake results in an increase in the mineral dissolution potential of the water body. The change in dissolution potential can be determined readily via the MCL diagram, for example :

Considering dissolution of carbonated OPC by white water (see Table 5.1(c)), the average CO_2 uptake per cycle is 28 mg/ℓ as $CaCO_3$. This uptake of CO_2 affects the dissolution potential as follows :

For no CO_2 uptake :	Both Acidity and (Alkalinity - calcium) are zero, and the dissolution potential is about 14 mg/ℓ as $CaCO_3$.
For 28 mg/ℓ CO_2 uptake :	The Acidity is 28 mg/ℓ and (Alkalinity - calcium) is zero, and the dissolution potential is about 30 mg/ℓ as $CaCO_3$.

Comparing the CO_2 uptake by the white water surrounding the three cement concrete types, the CO_2 uptake is closely the same for the two uncarbonated cement concretes (i.e. uncarbonated OPC and 30% fly ash OPC) with average uptakes of 27 and 23 mg/ℓ as $CaCO_3$ respectively. These uptakes are about 10 mg/ℓ, or 60%, greater than those by carbonated OPC. Similarly the uptake of CO_2 by the brown waters surrounding the three cement types is closely the same for the two uncarbonated cement concretes with average uptakes of 37 mg/ℓ and 33 mg/ℓ for uncarbonated OPC and 30% fly ash OPC. In this instance these uptakes are about 24 mg/ℓ higher than CO_2 uptake by the carbonated OPC. For both white and brown water the greater CO_2 uptake by the uncarbonated cement concretes results in a concomitant increase in the mineral dissolution potential compared with the carbonated specimens.

The higher CO_2 uptake for the uncarbonated specimens probably has minimal affect on the dissolution rates - this observation is arrived at by comparing the dissolution results between white water and brown water for a particular cement concrete type. Such a comparison reveals that although the brown waters contain initial Acidity (about 9 mg/ℓ as $CaCO_3$), whereas the initial Acidity of the white water is zero, similar dissolution rates per cycle occur once steady dissolution rates are attained.

With regard to (b) above, i.e. the effect of CO_2 uptake and possible calcium carbonate precipitation on the accuracy of dissolution assessment :

(i) For carbonated specimens uptake of CO_2 by the aqueous phase from the gaseous phase cannot cause precipitation of calcium carbonate in the aqueous phase. This is because the dissolving mineral is calcium carbonate and therefore calcium levels have an upper limit equal to the dissolution potential; carbon dioxide uptake by the aqueous phase simply increases this upper limit. The problem of calcium mineral dissolution underestimation will not occur for carbonated specimens.

(ii) For the uncarbonated specimens (where the dissolving mineral is lime) CO_2 uptake may cause concomitant precipitation of $CaCO_3$ from the aqueous phase. When pure distilled water is in contact with lime, but isolated from CO_2 in the air, dissolution will occur until a dissolved calcium level of about 2 300 mg/ℓ as $CaCO_3$ is reached. However, if CO_2 uptake occurs the introduction of the carbonate species means that the dissolved calcium concentration will now be limited to the solubility of $CaCO_3$. Where this is exceeded as a result of continued lime dissolution, concomitant precipitation of $CaCO_3$ out of the aqueous phase occurs.

The resulting calcium carbonate precipitation, and concomitant loss of both dissolved calcium and Alkalinity, gives rise to a corresponding underestimation of the lime dissolved. The degree to which the above occurs cannot be assessed from chemical consideration of the aqueous phase, however, an analysis of chemical water characteristics via the MCL diagram gives the saturation state of the water body with respect to calcium carbonate and hence whether precipitation is likely to have occurred.

An analysis of the results pertaining to uncarbonated cement concretes for white water shows that a calcium carbonate precipitation potential exists throughout the investigation for uncarbonated OPC. A similar analysis of the 30% fly ash OPC results shows that once steady state dissolution rates were attained, unlike the uncarbonated OPC, the water characteristics are such that $CaCO_3$ precipitation will not occur, i.e. undersaturation with respect to $CaCO_3$ still exists. Thus the error associated with monitoring of calcium mineral dissolution as a result of CO_2 uptake and concomitant $CaCO_3$ precipitation only applies to uncarbonated OPC once steady state dissolution rates occur. It is, therefore, accepted that dissolution of 30% fly ash OPC cement concrete has been accurately monitored whilst dissolution of uncarbonated OPC has been <u>underestimated</u> by some unknown amount.

In conclusion the following can be stated :

(a) Generally uncarbonated OPC cement concrete experiences higher calcium mineral dissolution rates than both 30% fly ash OPC and carbonated OPC cement concretes.

(b) Once steady dissolution rates were attained measurements indicated that 30% fly ash OPC and carbonated OPC cement concrete underwent closely the same calcium mineral dissolution rates.

(c) Uptake of gaseous carbon dioxide by the aqueous phase occurred throughout the investigation. This resulted in supersaturation with respect to $CaCO_3$ in the uncarbonated OPC tests; indeterminable comcomitant precipitation of $CaCO_3$ occurred with the uncarbonated OPC specimens causing an underestimation of calcium mineral dissolution per cycle. However, this reinforces the observation in (a) above that generally uncarbonated OPC experiences higher calcium mineral dissolution rates than both 30% fly ash OPC and carbonated OPC.

(d) The above observations apply to both white and brown water results.

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SECTION A

CHAPTER 6

GENERAL CONCLUSIONS

6.1 CONCLUSIONS

This section of the investigation had the principal objective of testing the hypothesis that carbonation of OPC concrete reduces the rate of subsequent attack by aggressive waters. This was achieved by comparing the dissolution rates in aggressive waters of uncarbonated OPC, carbonated OPC and 30% fly ash OPC.

The aggressive waters considered were a local brown water rich in humic substances and a distilled water.

In the experimental investigation, detailed in Chapter 5, calcium mineral dissolution rates were studied by exposing cement concrete specimens to aggressive water in dissolution tanks. The system was operated in "fill and draw" cycles with a hydraulic retention time per cycle of three days, up to a total time of exposure of about one hundred days. From these studies it was possible to compare the ability of the three cement concrete types to withstand aggressive attack by brown and white water. These comparisons revealed the following :

(a) Controlled accelerated gaseous carbonation of OPC concrete prior to exposure of specimens to aggressive water results in significant reduction in subsequent calcium mineral dissolution rates.

(b) Carbonated OPC and 30% fly ash OPC exhibited closely similar rates of aggression once steady state dissolution conditions were attained.

(c) The trends observed in (a) and (b) above occurred for exposure of cement concrete types to both brown and white water.

(d) Dissolution results obtained cannot be directly extrapolated to predict rates of aggressive attack of cement concrete conduits; likewise the results cannot be used to predict the precise ability of the different cement concrete types considered to resist aggressive attack. This is a result of the artifical nature of the tests which made use of "exposure cycles" of three days which resulted in significant change of state of raw water characteristics in a particular cycle. Nevertheless, the results can be used to identify the trends described in (a) to (c) above.

The investigation indicates that the use of (accelerated) carbonation of cement type conduits and water containing structures should be considered as means of extending the life of such conduits and structures where stabilization of transported or contained aggressive raw water is impractical.

6.2 RECOMMENDATIONS

The major finding of this section of the investigation is that both carbonated OPC and 30% fly ash OPC concrete have a significantly greater ability to resist aggressive attack than uncarbonated OPC. However, before these findings are implemented in practice (with the view of extending the life of cement concrete transporting or containing aggressive waters) a number of factors should still be investigated, including :

(a) An ecomonic and practical comparison of the relative benefits in using carbonated OPC and fly ash OPC as a means of reducing aggressive attack in water transporting/containing cement structures where stabilization of the raw water is impractical.

(b) An assessment of the relative ability of carbonated OPC and fly ash OPC to resist aggressive attack in pipelines transporting aggressive waters. In this regard it is suggested that changes in water quality be monitored in a pilot scale pipe network; change in water quality reflecting dissolution characteristics are most probably most sensitively reflected by changes in the $CaCO_3$ dissolution potential of the transported water.

(c) Investigation in (b) above should be extended to include carbonated fly ash OPC as an alternative, noting that both carbonation and fly ash incorporation contribute to reducing aggression.

(d) The desirability of carbonating large diameter reinforced concrete cement pipes with regard to increasing corrosion potential of steel reinforcing due to decreases in pH of the cement concrete pore water.

SECTION B

CHAPTER 7

CARBONATION OF CEMENT CONCRETE

7.1 INTRODUCTION

Section A of this investigation has shown that a calcium carbonate surface layer on cement concrete (in our case brought about via "accelerated carbonation") reduces the rate of attack by aggressive water on cement concrete. The findings indicate that the formation of such a carbonated layer in, for example, cement concrete pipes, is desirable where the conduit will be carrying aggressive water. This raises the question of effecting such carbonation in the practical situation.

Carbonation of cement concrete occurs naturally under normal atmospheric conditions; however, it is extremely slow, being in the order of 10 mm in 15 years for good quality concrete (Fulton, 1977). Hence in the practical situation an accelerated means of bringing about such carbonation is required. This can be achieved by exposing the cementitious material to carbon dioxide partial pressures significantly higher than that of the atmosphere (0,00035 atmospheres): such an approach is termed accelerated carbonation (Ho and Lewis, 1987; Dhir *et al*, 1985). However, practical implementation of acceleration carbonation requires a thorough understanding of the mechanism of carbonation and factors influencing its rate.

With regard to rate of carbonation the literature shows that it is significantly influenced by both cement concrete properties and environmental conditions (Moore, 1988; Parrot, 1987). Usually the cement concrete properties are fixed having been established to satisfy structural strength requirements. With regard to environmental effects, investigators have shown that carbonation rate will depend on a number of factors, *inter alia* the partial pressure of carbon dioxide and the curing regime prior to carbonation. Generally, it has been found that the carbonation rate increases with increase in partial pressure of carbon dioxide. However, reports on the influence of curing regime are contradictory in so far as the influence of water curing period (prior to carbonation) rates are concerned whilst no reports on the influence of air curing period were found.

The objective of this section of the investigation is to enquire into the influence of curing regime on subsequent accelerated carbonation. Clearly such an investigation requires an understanding of the mechanism of carbonation and factors influencing the rate of carbonation. This section, therefore, includes the following chapters :

Chapter 8 : Carbonation of Portland cement materials

Chapter 9 : Rate of carbonation

Chapter 10 : Experimental investigation into the influence of curing regime on accelerated carbonation

Chapter 11 : General conclusions.

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SECTION B

CHAPTER 8

CARBONATION OF PORTLAND CEMENT MATERIALS

8.1 THE STRUCTURE AND COMPOSITION OF PORTLAND CEMENT

Portland cement is the most important type of cement used for all forms of construction (Schlenker, 1981). The various types of Portland cement (e.g. ordinary, rapid hardening, low heat) all consist mainly of lime, magnesia, silica and alumina. While the composition of the cement powder can be analysed into oxide components, as in Table 8.1, Portland cement's actual chemical composition is a mixture of four predominant minerals. These are tricalcium silicate ($3\ CaO.SiO_2$), dicalcium silicate ($2\ CaO.SiO_2$), tricalcium aluminate ($3\ CaO.A\ell_2O_3$) and tetracalcium alumino-ferrite ($4\ CaO.A\ell_2O_3.Fe_2O_3$) (see Table 8.2). In addition to the main components there exist minor compounds such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O ; these usually amount to not more than a few per cent of the weight of cement (Neville, 1981).

TABLE 8.1 : Approximate composition limits of Portland Cement (from Neville, 1981)

Oxide	Content, percent
CaO	60-67
S_iO_2	17-25
$A\ell_2O_3$	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis	0.2-1.3
SO_3	1-3

TABLE 8.2 : Oxide and compound compositions of a typical Portland Cement (from Neville, 1981)

Oxide Composition	Percent	Compound Composition	Percent
CaO	63	$3CaO.SiO_2$	10.8
SiO_2	20	$2CaO.SiO_2$	54.1
$A\ell_2O_3$	6	$3CaO.A\ell_2O_3$	16.6
Fe_2O_3	3	$4CaO.A\ell_2O_3.Fe_2O_3$	9.1
MgO	1.5	Minor compounds	-
SO_3	2		
K_2O	0.5		
Na_2O	0.5		
Others	1		
Loss on ignition	2		
Insoluble residue	0.5		

The setting reactions of Portland cement are such that in the presence of water the main compounds set by a series of complex hydration reactions to produce the hardened cement paste. The setting reactions may be represented as follows (Schlenker, 1981) :

$$2\,(3\,CaO.SiO_2) + 6\,H_2O = 3\,CaO.\,2SiO_2.3H_2O + 3\,Ca(OH)_2 \qquad (8.1)$$

tricalcium silicate hydrate

$$2\,(2\,CaO.SiO_2) + 4\,H_2O = 3\,CaO.2\,SiO_2.3\,H_2O + Ca(OH)_2 \qquad (8.2)$$

tricalcium silicate hydrate

$$4\,CaO.A\ell_2O_3.Fe_2O_3 + 10\,H_2O + 2\,Ca(OH)_2 = 6\,CaO.A\ell_2O_3.Fe_2O_3.12\,H_2O \qquad (8.3)$$

calcium alumino-ferrite hydrate

$$3\,CaO.A\ell_2O_3 + 12\,H_2O + Ca(OH)_2 = 3\,CaO.A\ell_2O_3.Ca(OH)_2.12\,H_2O \qquad (8.4)$$

tetracalcium aluminate hydrate

$$3\ CaO.A\ell_2O_3 + 10\ H_2O + \underset{\text{gypsum}}{CaSO_4.2H_2O} = \underset{\text{calcium monosulpho-aluminate}}{3\ CaO.A\ell_2O_3.CaSO_4.10\ H_2O} \qquad (8.5)$$

When considering the above reactions it should be realised that the knowledge of the hydration products is far from complete and that the above equations are over-simplifications (Fulton, 1977). While the structure and appearance of the product calcium hydroxide are relatively well known, there is a lack of information and knowledge about the chemical composition and structure of the calcium silicate hydrates and calcium aluminate hydrates (Melzer and Eberhard, 1989; Shebl *et al*, 1985; Fulton, 1977). The calcium silicate hydrate product of Equations (8.1 and 8.2) is often referred to as tobermorite gel because of its structural similarity to the natural mineral tobermorite. However, recent research has shown that the hydration mechanism of calcium silicate (which makes up approximately 50% of the bulk of the set cement and very largely determine its strength properties) is considerably more complicated than suggested by Equations (8.1 and 8.2). The hydration is reported to comprise of a range of phases of differing compositions depending on such factors as time, temperature and w/c ratio (Neville, 1981; Shebl *et al*, 1985; Suzuki *et al*, 1985). Shebl *et al*, 1985 found that the hydration of calcium silicates can be divided into five different stages with the calcium silicate ratio varying throughout. (For an in-depth description of these stages see Shebl *et al*, 1985). However, Melzer and Eberhard (1989) in surveying the literature report that several contradictory data exist regarding the composition of calcium silicate hydrates. Due to these variances the calcium silicate hydrates are generally referred to as C-S-H and Equations (8.1 to 8.5) are not to be regarded as stoichiometric but rather as a guide to the hydration process (Neville, 1981; Fulton, 1977).

In addition to the hydrates of the various compounds and the $Ca(OH)_2$ crystals the cement paste also consists of water filled spaces known as capillary pores. As the reactions and equilibria in cement are complicated and not well defined a theoretical quantitative estimation of the pore solution composition at a given time is impossible (Andersson *et al*, 1989). Experimental results by Andersson *et al*, 1989 report the ionic strength, pH, Eh and cation composition of pore solutions from pastes using seven different cement types (see Table 8.3). His results showed that the main cations present in the pore water of portland cement are K, Na, and Ca. The cement pore solution has fairly high ionic strengths (up to 0.3), pH in the range of 12.4 to 13.5, and positive redox potentials (except for the slag containing blast furnace cement and the French Portland cement). For both the standard Portland cements considered (i.e. French and Swedish) the dominant cations were Na (± 17 00 mg/ℓ on average) and K (± 60 000 mg/ℓ on average), and the pH was on average approximately 13.3. Lea (1970) notes that the pore water is often supersaturated with respect to calcium hydroxide.

TABLE 8.3 : Data for the pore water of seven cement pastes (from Andersson *et al*, 1989)

	SPP	CPA	SRP	MP	ALP	FAP	SIP
volume	8	4	9	9	7	8	4
age	10	4	9	10	10	10	10
w/c	0.5	0.36	0.5	0.5	0.5	0.5	0.35
Na	1500	1800	800	3200	4200	1600	300
K	6300	5700	800	6000	100	7500	700
Ca	90	20	470	50	1	15	130
Mg	0.2	0.1	0.2	0.1	0.06	0.15	0.1
Al	5	30	5	5	2800	15	5
Si	6	6	6	6	6	6	6
Fe	0.5	0.5	0.5	0.5	0.9	0.7	0.5
Icalc	0.23	0.22	0.04	0.29	0.18	0.26	0.03
Eh	139	-196	84	-377	131	106	134
pH	13.4	13.2	13.1	13.5	13.3	13.4	12.4

where : volume = volume pressed from 0,2 kg solid, ml

age = age before pressing, months

$I = 0,5 \sum C_i Z_i^2$, moles

Eh is in mV

SPP = Swedish standard OPC

CPA = French OPC

SRP = Sulphate resistant cement

ALP = High alumina cement

FAP = Fly ash cement (30%)

SIP = Silica cement

8.2 THE CARBONATION PROCESS

In practice cement is sufficiently permeable to allow penetration of carbon dioxide from the atmosphere. The gaseous carbon dioxide dissolves readily into the alkali pore water and subsequently reacts with the products of hydration to form mainly calcium carbonate minerals. It was initially thought that only the calcium and hydroxide species produced by the hydration of C-S-H were susceptible to carbonation (Fulton, 1977). It has since been shown that virtually all the hydrates and the alkali hydroxides in the cement paste can react with dissolved carbonate species in equilibrium with atmospheric carbon dioxide (i.e. at a carbon dioxide concentration of 0.03% by volume) (Parrot, 1987). There is disagreement in the literature as to whether calcium hydroxide or C-S-H in cement material is more susceptible to carbonation. Rearden (1989) reports that Venuat & Alexandre (1968) and Calleja (1980) both conclude that calcium hydroxide is the more active component. However, Slegers and Rouxhet (1976) suggest that C-S-H is the more reactive phase, pointing to such evidence as the presence of unreacted calcium hydroxide in carbonated samples in which the C-S-H phase has been fully carbonated.

The principal reactions of hydrated cement with carbon dioxide as cited by Cole and Kroone (1960) and Hobbs (1988) are :

$$\text{C-S-H}_{(s)} + CO_{2(g)} \rightarrow CaCO_3 + \text{Silica} + H_2O_{(\ell)} \qquad (8.6)$$

$$Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_3 + H_2O_{(\ell)} \qquad (8.7)$$

These equations are an oversimplification of the carbonation process and it is necessary to elaborate on the sequence of chemical reactions. The reactions which take place can be conveniently separated into two different processes, i.e.

(a) supersaturation and concomitant precipitation of $CaCO_3$ in the pore water <u>and</u>

(b) carbonation of the hydrates.

Both of these processes are discussed in more detail below :

(a) Supersaturation and precipitation of $CaCO_3$ in pore waters

As ambient carbon dioxide diffuses into the cement matrix via the capillary pores it comes into contact with the free water within these pores. In fresh cement (ie. before carbonation) the pore water has a minimum pH of 12.6 (due to the presence of excess solid calcium hydroxide), but can have a pH of up to 14.0 (due to the dissolution of sodium and potassium hydroxides) (Hobbs, 1988). This pore water has high alkalinity and negative acidity and, as such, gaseous carbon dioxide is extremely soluble (see Chapter 3).

The diffusion of carbon dioxide into the cement matrix results in the uptake of substantial amounts of carbon dioxide by the pore water, a corresponding drop in pH (causing $CaCO_3$ supersaturation and precipitation) and eventually the attainment of 3-phase equilibrium at a pH of about 8.4. The overall process can be represented stoichiometrically by Equation 8.7, i.e.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Powers (1962) pointed out that the calcium hydroxide cannot convert to calcite or aragonite in situ because its conversion is related to an increase in volume. Since calcium hydroxide is completely surrounded by and attached to C-S-H, if it is converted in situ, the related volume expansion would burst the cement paste. Moorhead (1986) proposed that subsequent to the initial CO_2 uptake and consequent precipitation of $CaCO_3$ as described by Equation (8.7), further dissolution of $Ca(OH)_2$ crystals occurs under the acidified conditions resulting in a repeat of the cycle and further precipitation. This process would proceed until all the hydroxide particles are converted to carbonate or until the water used as the vehicle for the reaction was evaporated due to the heat of reaction. The following reaction sequence can thus be envisaged :

(i) Supersaturation of pore water with $Ca(OH)_2$ resulting in the pore water having the characteristics of high alkalinity, high pH and high negative acidity.

(ii) Uptake of gaseous CO_2 into the pore water causing an increase in Acidity, a drop in pH and $CaCO_3$ supersaturation. (Alkalinity remains constant.)

(iii) $CaCO_3$ precipitation from supersaturated water causing a decrease in Alkalinity and pH. (Acidity remains constant.)

(iv) Further dissolution of $Ca(OH)_2$ in the acidified solution resulting in a repeat of steps (i) to (iv).

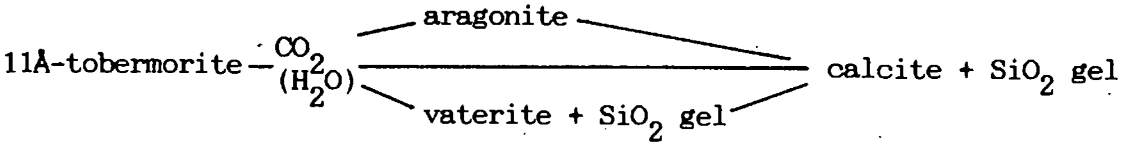
(v) The above process continues until all the soluble calcium hydroxide is converted to calcium carbonate, or until the heat generated by the reaction evaporates all the water used as the vehicle for the reaction.

This reaction sequence follows a similar pattern to that proposed by Moorehead (1986). He noted that the calcium carbonate precipitated is mainly micro crystalline or amorphous forms of calcium carbonate.

(b) Carbonation of the hydrates

The chemical process by which carbonation of the various hydrates occurs (i.e. the changes in the liquid and solid phases) has not been clearly determined (Suzuki *et al*, 1985). However, it is known that the atmospheric carbon dioxide only can react with the cement hydrates when there is sufficient pore water for carbon dioxide dissolution from the gas phase (Parrot, 1987; Rearden *et al*, 1989). It is also known that the products of this reaction between the main cement hydrates (i.e. calcium silicate hydrate, and various calcium or ferro-aluminate hydrates) and the aqueous carbonate species are calcium carbonate (both solid and dissolved), silica gel, water and iron oxides (Parrot, 1987; Hobbs, 1988 and Rearden *et al*, 1989).

Although all the main hydrates are susceptible to reactions with dissolved carbonate species (Parrot, 1987) most of the specific research on the chemistry of the process would appear to have been carried out on the calcium silicate hydrates; these are the chief cementing and hardening agents in Portland cement (Sauman, 1971; Suzuki *et al*, 1985). Cole and Kroon (1960) report that solid calcium carbonate precipitated during carbonation of hydrates is poorly formed vaterite, aragonite and calcite. Sauman (1971), using X-ray diffraction and infra-red spectrometry, examined the changes to C-S-H and again found that the products were the calcium carbonate allotropes vaterite, aragonite and calcite, and silica gel. The relative fractions of these allotropes was shown to be influenced by such factors as period of exposure, partial pressure of gaseous carbon dioxide and relative humidity, but that vaterite and aragonite were unstable intermediate products which were not evident one year after carbonation. He modelled the reaction sequence of 11Å-tobermorite (a calcium silicate hydrate) as follows :



It was noted that the principal calcium carbonate intermediate was vaterite and aragonite only occurred to a "relatively very small extent". As regards the influence of the partial pressure of the gaseous carbon dioxide and the relative humidity, it was shown that the formation of vaterite is inversely proportional to both the carbon dioxide partial pressure and the ambient relative humidity. That is the formation of vaterite mainly depends on a relatively lower carbon dioxide partial pressure (0.01 - 0.1 atmospheres) and on a moderate relative humidity (50% - 75%). Calcite is observed to occur almost exclusively in a medium of 100% relative humidity at relatively high CO_2 partial pressures (> 0.1 atmospheres).

Sauman also studied the morphology (outer structure) of crystalline C-S-H prior to and during carbonation with the aid of an electron microscope. He observed that the original C-S-H (11Å-tobermorite) crystals prior to carbonation are characterized by rod and flat plate-shaped crystals. He reported that no changes in the morphology of these crystals was visible over the first thirty days of exposure to 0.1 bar carbon dioxide at a relative humidity of 75%. After a storage period of half a year and longer in an environment of 0.3 atmospheres carbon dioxide and 100% relative humidity the crystals were only "somewhat thinned". After a one year exposure period the change in particle morphology was not considerable and the external basic shape of the crystals was maintained even though analyses revealed high concentrations of calcium carbonate allotropes. Saumann stated that from these observations it follows that a pseudomorphis occurs whereby there is gradually formed in the mass of the C-S-H crystal, calcite or its mixture with vaterite or aragonite simultaneously with the formation of SiO_2 gel. Slegers and Rouxhet (1976) used X-ray diffraction and infra-red spectraphotometry to also identify all three allotropes of calcium carbonate present in the carbonated hydrates. These observations would appear to be generally accepted in later literature (Parrot, 1987; Rearden, 1989).

Baird *et al* (1975), using electron microscopy, also observed virtually no changes in the external morphology of the C-S-H crystals. However, in contrast to the other researchers, by using infra-red spectrometry they could find no evidence of calcium carbonate crystals within the carbonated C-S-H products. This led them to the hypothesis that carbonation leads to the formation of calcium and carbonate ions which remain in "solution" in a "solvent" of cross-linked silica gel, (i.e. the solubility product for the calcium carbonate crystals is not exceeded within this silica gel "solvent".) Such a process they state would not significantly effect the silicate anion structure, thus maintaining the observed C-S-H pseudomorphis.

Rearden (1989) proposed that the overall carbonation reaction of C-S-H is the result of interactions between three phases :

- a gas phase in which carbon dioxide is present;
- an aqueous phase comprised of pore water and thin alkaline film coating the cement pores and particles, termed adsorbed water;
- and a solid phase comprised of the C-S-H minerals.

The carbonation of C-S-H can thus be seen to occur in the following sequence :

Stage One :
Diffusion of carbonate species into the adsorbed water; either from carbon dioxide in the gas phase or from aqueous carbonate species in the pore water.

Stage Two :
Diffusion of carbonate species from the adsorbed water into the C-S-H crystals.

Stage Three :
Internal crystal carbonation reactions (i.e. equation 1) in a pseudomorphic frishon with concomitant release of water into the pore interstices.

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SECTION B

CHAPTER 9

RATE OF CARBONATION

9.1 FACTORS INFLUENCING RATE OF CARBONATION

Carbonation of concrete usually occurs very slowly. With good quality concrete the rate of carbonation is in the order of ± 10 mm in 15 years (Fulton, 1977). This is as a result of the low partial pressure of carbon dioxide in the atmosphere and the low permeability of concretes of normal cement content. However, with poor quality concrete under similar exposure conditions carbonation depth in the same period may be three to four time greater. Due to these large variances, it is necessary to identify the principal factors which influence carbonation rates. Where concrete is not protected by surface coatings the principal factors influencing carbonation rates are :

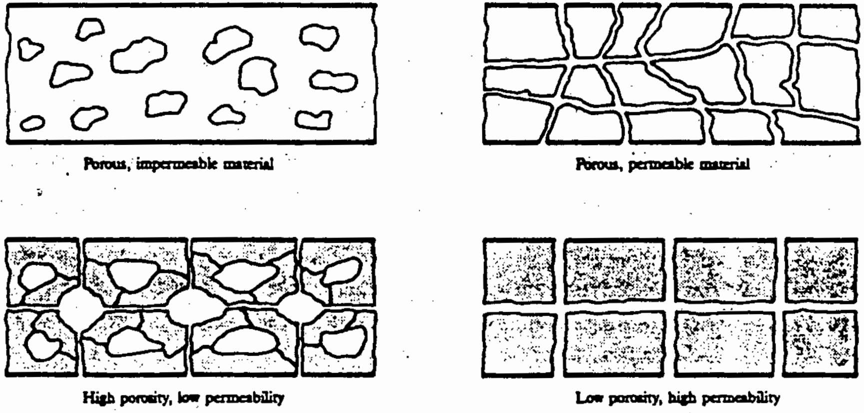
(1) permeability and
(2) atmospheric conditions (Moore, 1988).

9.1.1 Permeability and cement properties

Carbonation is a diffusion process. Consequently it is often stated that the permeability of the concrete is the single most important factor influencing the rate and extent of carbonation under atmospheric conditions (Moore, 1988). Hence, it is important that the concept of permeability, which is also sometimes confused with porosity, be clearly defined (see Figure 9.1).

'Porosity' is a volume property and represents the content of pores which are not necessarily inter-connected and may not, therefore, allow the passage of fluid or gas.

'Permeability' is a flow property and is defined as that property of a porous medium which characterises the ease with which a fluid or gas will pass through it, under the action of a pressure differential.



Porous, impermeable material

Porous, permeable material

High porosity, low permeability

Low porosity, high permeability

Figure 9.1 : Illustration of permeability and porosity.

From this general definition the term "permeability" applies specifically to the property of flow of a gas or fluid under a total pressure differential. This is seldom the circumstance during carbonation where the driving force is usually the action of a concentration gradient, i.e. a diffusion process. However, in most instances describing the carbonation process, the terms permeability and diffusivity are used interchangeably. Possibly, the reason for this is that these two properties are linearly related for cement materials (Lawrence, 1981). Thus a cement or concrete described as having a low permeability will also have a low diffusivity and, therefore, although not technically correct, the use of the term permeability when describing the relative potential for carbonation need not be misleading.

The permeability (or diffusivity) of concrete is not a simple function of its porosity. It depends also on the size, distribution, and continuity of the cement pores and voids and, to a lesser extent, the properties of the aggregate.

According to Neville (1981) permeability (and thus the carbonation rate) will depend principally on the characteristics of the cement paste which envelopes the aggregate particles; and the influence of the aggregate in the mix is generally small. Before considering those factors which most

The permeability of cement paste varies considerably with the curing period; the longer the curing period the less permeable is the cement for a particular mix design (Powers *et al*, 1955). Powers explained this observation as follows :

In a fresh paste, the flow of water is controlled by the size, shape and concentration of the original cement grains. With the progress of hydration the permeability decreases rapidly. This arises because the gross volume of the products of hydration (gel) are approximately 2,1 times the volume of the unhydrated cement, consequently the gel formed gradually fills the original water filled space. In a mature paste (i.e. after the hydration reactions have taken place), the permeability will depend, therefore, on the size, shape and concentration of the gel particles and on whether or not the capillaries have become discontinuous. These observations are illustrated in Figure 9.2 (Ho and Lewis, 1987) which indicates a decrease in permeability with increase in curing period.

The influence of curing on subsequent carbonation rates is likely to be similar to that on permeability, i.e. with increased curing period a decrease in carbonation rate (for a particular mix). This arises because, as stated earlier, carbonation depends on diffusivity and diffusivity is directly linked to permeability. Data on the influence of different curing regimes on subsequent rate of cement carbonation are sparse (Fattuhi, 1988). However, work by Nagataki *et al* (1986), Ho and Lewis (1987) and Fattuhi (1986), show that indeed an increase in water curing period decreases subsequent carbonation rates (see Figure 9.3). Ho and Lewis (1987) and Nagataki *et al* (1986) found that carbonation rates decreased with increase in curing period up to seven days, but remained practically unaffected for a curing period greater than seven days.

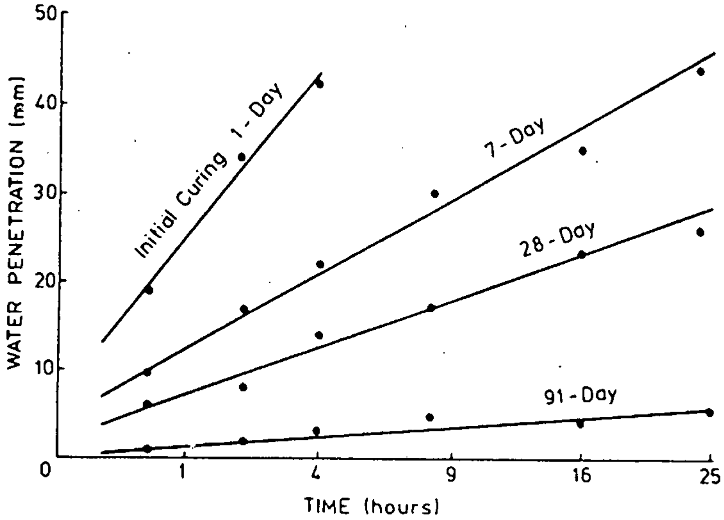
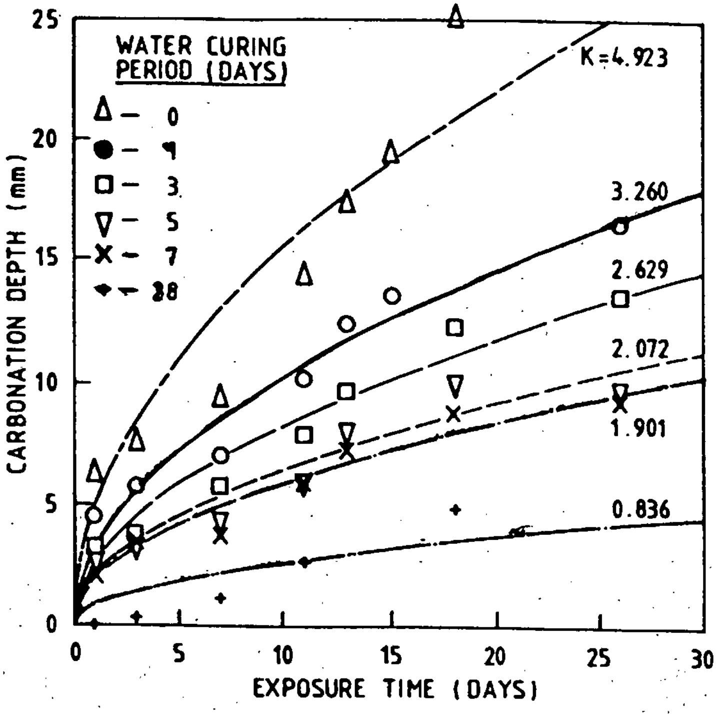


Figure 9.2 : Influence of initial water curing period on the water penetration of plain concrete (from Ho and Lewis, 1987).



(b) Mix design

The values of the water/cement ratio, cement content and aggregate grading used in a mix design all have an influence on the permeability of the mature concrete. Of these parameters the water/cement ratio dominates (Parrot, 1987). The lower the water/cement ratio (i.e. the higher the cement content), the lower is the permeability for concrete hydrated to the same degree. The degree of hydration is the relative extent to which the unhydrated cement has hydrated in the manner set out in Section 8.1. This arises from the higher cement content which leads to a larger volume of hydration products with a concomitant decrease in the volume of the capillary pores within the concrete (Fattuhi, 1986). The magnitude of this influence is shown in Figure 9.4 using data from Power *et al*, 1955. The plot shows that for cement pastes with the same degree of hydration a reduction in the water/cement ratio from 0,7 to 0,3 results in a decrease in the coefficient of permeability by three orders of magnitude. Consequently in practice the main parameter used to control permeability (and hence carbonation rate) is the water/cement ratio (Ho and Lewis, 1983; Fattuhi, 1986; Parrot, 1987).

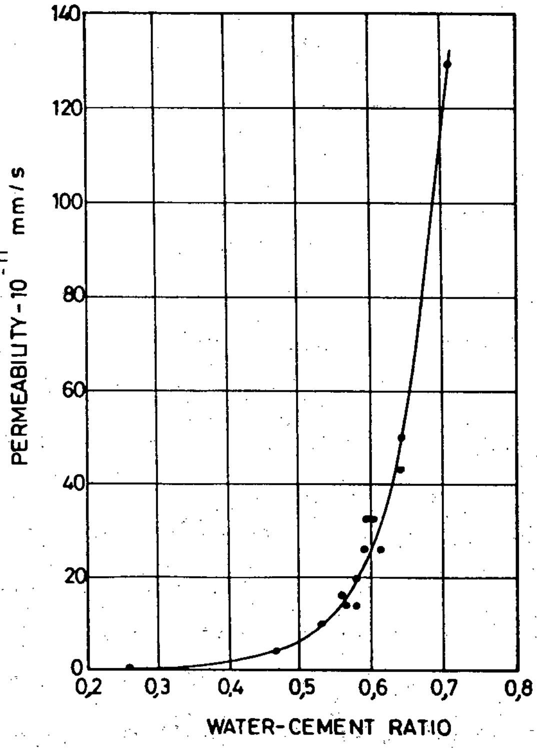


Figure 9.4 : The influence of water/cement ratio on the permeability of mature cement pastes (from Power *et al*, 1955).

resistance to carbonation from the two binders, OPC and fly ash, is different (Hobbs, 1988). Hobbs suggests that their relative influence on carbonation be separated out using a parameter termed "water/effective cement ratio", i.e. $w/(c + kp)$ where p is the fly ash content and k is the mass of OPC which gives similar resistance to carbonation as a unit mass of fly ash. Hobbs has shown that the k value in this parameter varies between fly ashes and has small relative influence (i.e. the value of k is in the region of 0,1 to 0,2). Consequently, many researchers have suggested that the w/c ratio be regarded as a more universal parameter for describing carbonation resistance even when cement extenders are used (Ho and Lewis, 1987; Parrot, 1987).

(ii) Water/cement ratio

As discussed earlier, it has been shown that for mixes that contain no cement extenders a reduction in w/c ratio will result in a reduction in carbonation rate (Fattuhi, 1987). Ho and Lewis (1987) extended this by showing that for a range of fly ash mixes (0 to 40%) the water/cement ratio has an excellent correlation with carbonation depth (see Figure 9.6). This implies that for cements to have identical carbonation resistance, the percentage of cement reduction cannot be greater than the percentage reduction of water brought about by the incorporation of fly ash. These observations are in agreement with Parrot (1987) and support the use of the w/c ratio for judging relative resistance to carbonation even when cement extenders are used.

(iii) Compressive strength

An alternative and popular approach when considering the potential rate of carbonation is in terms of the 28 day compressive strength of the mix. Parrot (1987) notes that a large number of researchers have shown that an increase in 28 day compressive strength results in a pronounced reduction in the rate of carbonation of ordinary Portland cement. In Figure 9.7 the relationship is shown between 28 days strength and rate of carbonation using data from Ho and Lewis (1987); the plot shows a

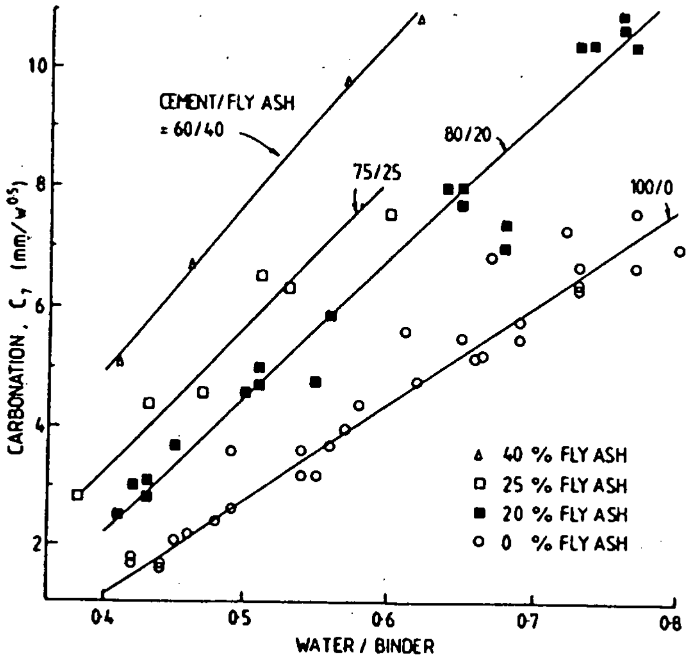


Figure 9.5 : Influence of water/binder ratio on the carbonation of concretes (from Ho and Lewis, 1987).

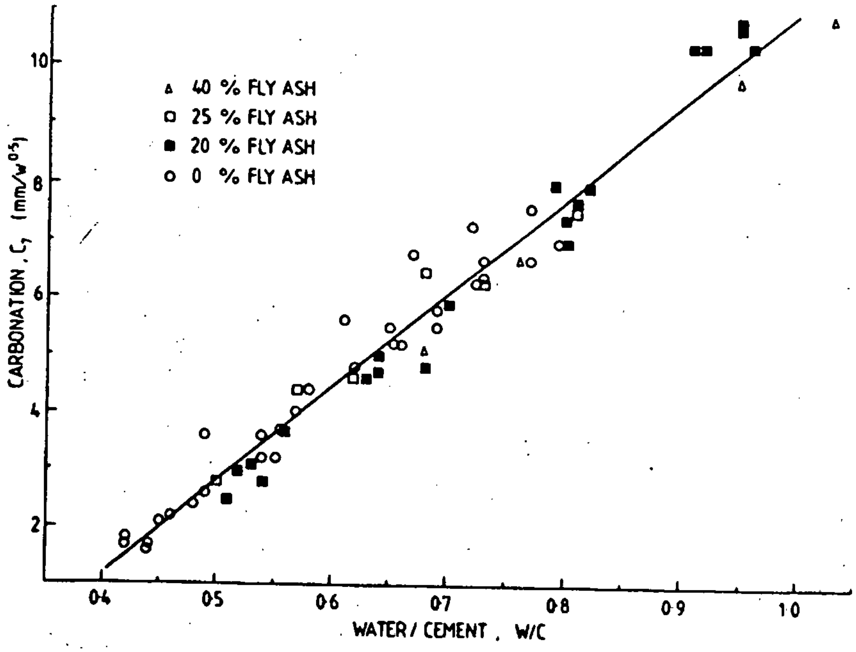


Figure 9.6 : Influence of water/cement ratio on the carbonation of concretes containing fly ash (from Ho and Lewis, 1987).

> closely linear relationship between 28 day strength and carbonation depth. Ho and Lewis also investigated the influence of fly ash/cement mixes and 28 day compressive strength on the rate of carbonation. They noted that in order to achieve similar resistance to carbonation an increased 28 day strength would be required for increasing fly ash percentages in the mix design. This observation is supported by Mathews (1984) and Tsukayama *et al* (1980). However, these observations are in disagreement with many other investigators who found that the use of fly ash has little effect on the carbonation rate for a given compressive strength, (Nischer, 1984; Hobbs, 1988).

It should be noted that the discussion above is in terms of present day cement properties. However, cement properties, and hence cement strength, undergo continued change as a result of advances to the manufacturing process (Moore, 1988). In USA, for example, cement strengths have more than trebled since 1916 resulting in a 40% reduction in cement content in concrete of the same strength class (Oberholster, 1986). Likewise, Moore reports that in the United Kingdom between 1945 and 1980 there has been a marked increase in the strength of concrete made with a given quality of cement. (See Table 9.1). Thus, as cement properties have improved, higher water/cement ratios (i.e. decreased cement content) have been used to achieve a required strength. This results in a more porous concrete with higher permeability and less resistance to carbonation. In the design of concrete for service in exposed conditions it is not sufficient to consider strength requirements only. Consequently, with the increasing permeability of modern cements it would appear necessary to choose the w/c ratio as an indicator to both strength and resistance to carbonation.

9.1.2 Atmospheric conditions

The main variables describing the ambient atmospheric conditions which influence carbonation rates are carbon dioxide concentration (i.e. partial pressure of carbon dioxide) and relative humidity; in addition the exposure conditions are of importance (i.e. whether the sample is exposed to cyclic wetting and drying). On average carbon dioxide comprises 0,03 percent of the atmosphere. However, the carbon dioxide

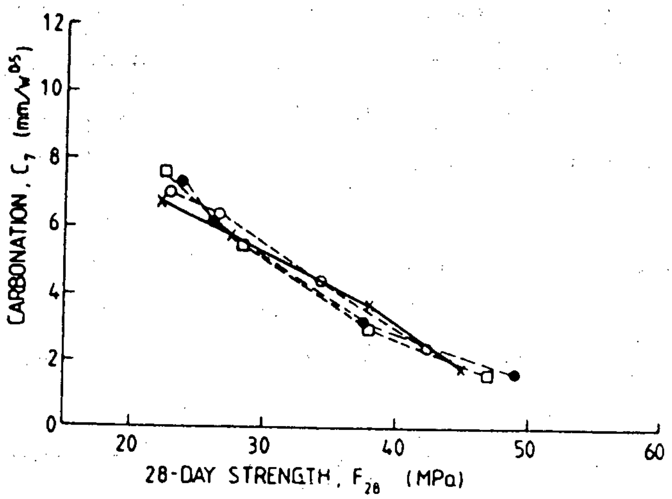


Figure 9.7 : Influence of 28-day compressive strength, F_{28} (MPa), on carbonation of concretes (from Ho and Lewis, 1987).

TABLE 9.1 : Changing strengths of Portland cement concrete in Great Britain. Cement content ca. 300 kg/m², w:c ratio 0,60 (from Moore, 1988).

Period	28-day strength in N/mm²
1945 - 1947	25,0
1948 - 1953	29,0
1954 - 1958	33,0
1959 - 1965	36,5
1966 - 1974	39,5
1975 - 1980	43,5

Variable moisture conditions, such as those that would be brought about by outdoor exposure, have been shown to influence the carbonation rate. Ho and Lewis (1987) found that, during one year of exposure, rates of carbonation obtained from outdoor exposure (i.e. variable conditions) were lower than their laboratory (i.e. constant conditions) counterparts. Even under outdoor conditions carbonation was found to vary; with vertical specimens carbonating faster than inclined specimens (see Table 9.2). It is likely that these differences are due to the inclined specimens receiving more rain than the vertical specimens (Ho and Lewis, 1987). These observations are in agreement with those discussed by Moore (1988). Moore found that concrete which is in direct contact with the outdoor atmosphere undergoes carbonation at a slower rate when it is kept moist or is subjected to cyclic wetting. Parrot (1987) states that the significant reduction in carbonation rate due to periodic wetting is a result of the slower rate of carbon dioxide diffusion through partially saturated pores of the cement paste matrix.

9.2 MODELLING OF CARBONATION RATES

According to Moore (1988) the fundamental empirical relationship modelling carbonation depth with time is :

$$d_c = \sqrt{(2 * D * C1 * t) / C_2} \qquad (9.1)$$

where d_c = depth of carbonation (mm)
D = diffusion coefficient of concrete (mm^2/time unit)
C1 = CO_2 concentration in the ambient environment (%)
C2 = requisite equivalent amount of CO_2 for reacting with calcium hydroxide contained in the concrete
t = time.

This equation takes into account the principal factors influencing carbonation rates, i.e. partial pressure of carbon dioxide, concrete characteristics and time. However, the model is not suitable for practical purposes as the values for the parameters (particularly D, C1 and C2) usually are not known. Consequently, more empirical approaches

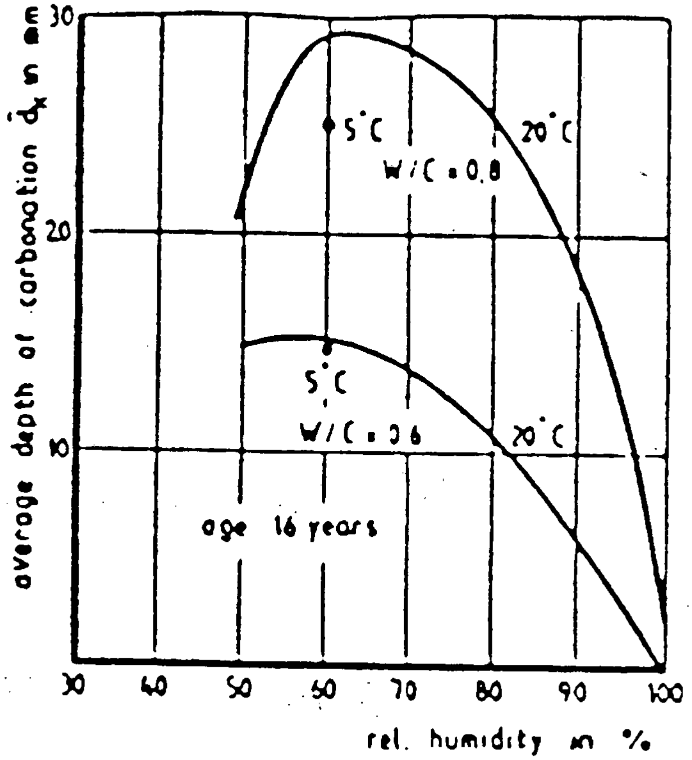


Figure 9.8 : Influence of relative humidity and water/cement ratio on carbonation of concretes (from Wierig, 1984).

TABLE 9.2 : Depths of carbonation (mm) of fly ash concretes after 21 days of drying followed by one year exposure (specimens initially cured for one day) (Ho and Lewis, 1987).

F_{28} (MPa)	After 21 days of air drying	21-day drying + one-year exposure		
		Laboratory	N vertical	S inclined
46	3,0	8,5	4,5	3,0
35	3,5	13,0	7,0	4,0
26	4,0	16,0	10,0	5,5
18	5,0	17,0	11,5	6,5

have been adopted in which modelling is in terms of alternative parameters the values of which are known and can be controlled, for example, water/cement ratio, water curing period and compressive strength. In the previous section it was shown that these three parameters are the principal parameters influencing the permeability of concrete which, in turn, governs carbonation rates. As such, one would expect to be able to empirically model carbonation rates in terms of any one of these parameters when atmospheric exposure conditions, such as relative humidity and carbon dioxide concentration, are kept constant. Numerous investigators, *inter alia* Nagataki, 1986; Le Sage de Fontenay, 1985; Fattuhi, 1987 have empirically modelled depth of carbonation with time under atmospheric concentrations of carbon dioxide using the water/cement ratio as the governing parameter. The authors all used approximately the same form of empirical expression but varied constants depending on the geographic region. For example, Le Sage de Fontenay (1985) proposed the following formulations for Bahrain conditions :

$$d_c = 0{,}43\ (w/c - 0{,}4)\ [12\ (t-1)^{0{,}5}] + 0{,}1 \tag{9.2}$$

and

$$d_c = 0{,}53\ (w/c - 0{,}2)\ [12\ t]^{0{,}5} + 0{,}2 \tag{9.3}$$

where Equation (9.2) is for samples cured for 28 days and Equation (9.3) is for non-cured samples.

Fattuhi (1987) proposed a similar relationship for exposure conditions in Kuwait :

$$d_c = [0{,}687\ (w/c) - 0{,}176]\ t^{0{,}5} \tag{9.4}$$

Hobbs (1988) extended this work by reporting on a limited investigation into the influence of the replacement of one OPC by two fly ashes (i.e. 35% fly ash to 65% OPC by mass) on depth of carbonation with time. When no fly ash was present he proposed a formulation of the same form as Fattuhi in Equation (9.4), i.e. :

$$d_c = (A\ [w/c] - B)\ t^{0{,}5} \tag{9.5}$$

However, he also noted that the resistance to carbonation of OPC and fly ash are different and can be modelled by the extension of Equation (9.5) :

$$d_c = (A\,[w/(c + 0{,}2\,P)\,] - B\,)\,t^{0{,}5} \qquad (9.6)$$

where t = exposure period
A,B = constants dependant on concrete quality and exposure conditions
w = water
c = cement
P = fly ash.

Each of these equations were found by the respective authors to satisfactorily predict measured carbonation rates.

Other investigators *inter alia* Fattuhi (1986), have made use of the initial water curing period as the governing parameter to formulate a model of the carbonation rate. Fattuhi (1986) found that for concrete initially cured in water for between 1 and 21 days the following empirical relationship exists :

$$d_c = 2a\,t^{0{,}5}\,(t_{wc})^{-b} \qquad (9.7)$$

where $a + b$ = constants that depend on concrete properties
t = the exposure period
t_{wc} = the initial water curing period.

Unfortunately, Fattuhi does not compare his two models, i.e. carbonation rate in terms of, firstly, the water/cement ratio as in Equation (9.4) and, secondly, in terms of water curing periods as in Equation (9.7). Further, recognising that the characteristics of concrete depend on both water/cement ratio and curing periods, one would have expected the development of a single model in terms of both of these parameters, i.e. encompassing both Equations (9.4) and (9.7).

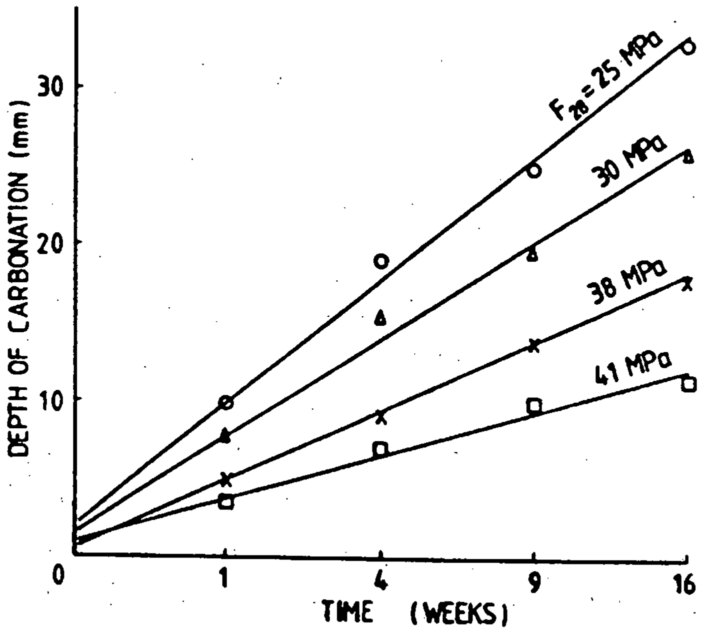
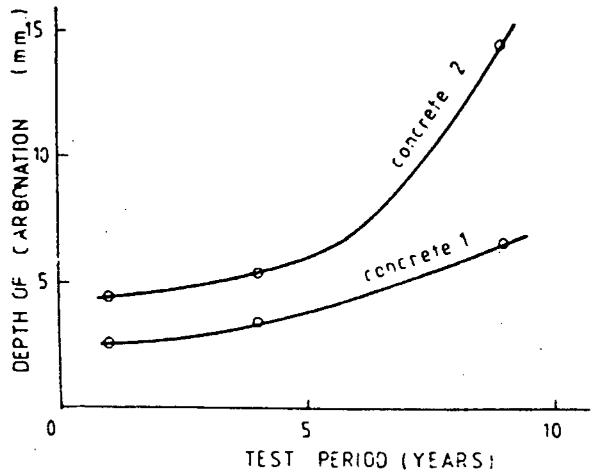


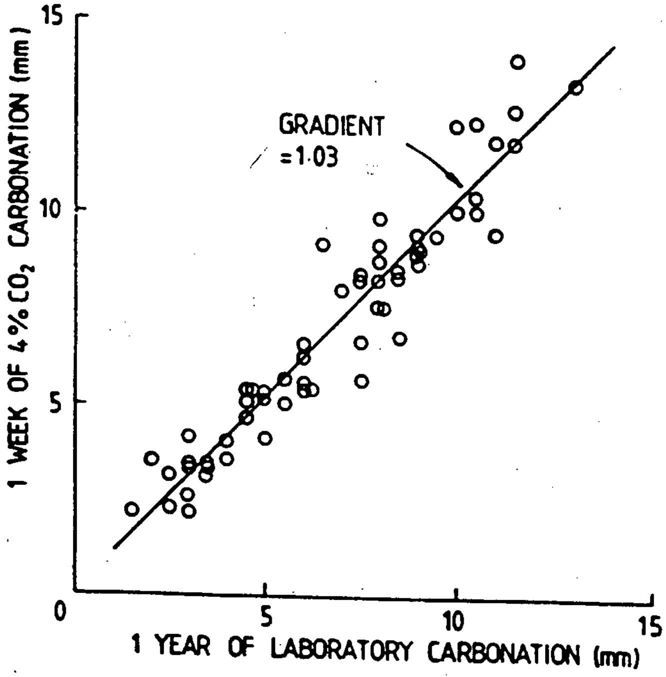
Figure 9.9 : Square root relationship between carbonation depth and time (from Ho and Lewis, 1987).

9.3 ACCELERATED CARBONATION

Carbonation under normal atmospheric conditions, i.e. where the partial pressure of carbon dioxide is usually about 3 x 10^{-4} (or 0,03% by volume) is a slow process for both structural strength concrete (10 mm in 15 years) and lower strength concrete (12 mm in 8 years). This creates a problem both in investigating the durability of concrete materials (i.e. the requirement for tests which can take years to complete) and in an instance such as in this investigation where a carbonated layer is desired. With regard to the former, the limitations of long term tests on carbonation rates and the advantages of accelerated short term tests have been discussed by Ho *et al* (1985) and Dhir *et al* (1985). Summarising their findings, the usefulness of long term results depends very much on whether or not materials used in the research program are still available on the program's completion. Very often by the time results are obtained the intrinsic properties of the cement or the cement extenders used have changed so that results cannot be meaningfully used.



<u>Figure 9.10</u> : Carbonation tests indicating that early extrapolation of carbonation data at normal atmospheric carbon dioxide partial pressure can be misleading (from Ho *et al*, 1985).



With regard to these factors, accelerated carbonation tests have shown that the carbonation rate is significantly influenced by the curing regime. Determining the influence of curing regime on carbonation rates is important principally for the following two reasons. Firstly, where control of carbonation and, particularly, accelerated carbonation is desired it is important to quantify the influence of varying curing regimes. Secondly, once the influence of curing regime on carbonation rates is known the influence of other variable parameters can be more accurately determined.

9.3.1 The influence of curing regime on accelerated carbonation

For a meaningful comparison of the influence of varying mix designs, admixtures and cement extenders on carbonation rates, it is necessary to ensure that the variability of external influencing parameters, such as curing regime and compaction, is minimized. As a degree of variability inevitably occurs between different investigations it is important to be able to assess the influence of these variances on carbonation rates. In particular, variance in curing regime is likely to have an influence on accelerated carbonation rates; unfortunately, data on the influence of different curing regimes on accelerated carbonation rates is sparse and inconclusive.

Ho and Lewis (1987) subjected samples to different water (fog) curing durations (1, 7, 28, 91 and 365 days), followed by conditioning in a laboratory at 23°C and 50% relative humidity (R.H.) for 21 days. Thereafter, samples were placed in a carbonation chamber with a controlled environment of 23°C, 50% R.H. and a partial pressure of carbon dioxide ($\bar{p}CO_2$) of 0,04 ± 0,005 atmosphere. A plot of their data using Equation (9.11) is shown in Figure 9.12. The plot shows that the carbonation rate decreased with increase in water curing duration up to 7 days but remained practically unaffected for further increase in water curing period. Ho and Lewis noted that similar findings were made by Nagataki *et al* (1986) for normal atmospheric exposure. Nagataki *et al* found that after 15 years of outdoor exposure, the depth of carbonation was greater for concretes water cured for 1 day compared with those cured for 7 and 91 days; the latter two being very similar.

Futtuhi (1988) carried out similar investigations into the influence of curing regimes on accelerated carbonation rates. His investigation was carried out by varying the period of water and air curing immediately after demoulding specimens. Fattuhi subjected samples to 1, 3, 5, 7 and 28 days water curing followed by an air curing period of a duration such that a total curing period prior to carbonation of 28 days existed. Fattuhi placed his samples at a total age of 28 days into a controlled environmnent of 20-26°C, 50-70% R.H. and a "full concentration" of carbon dioxide. In doing so he effectively also varied the dry curing (or drying out period) prior to carbonation and not only the water curing period. This is in contrast to Ho and Lewis (1987) who used a set air curing period regardless of water curing period. Fattuhi found that the rate of concrete carbonation continuously decreased with an increase in water curing period. A plot of his data given in Figure 9.13 shows that the carbonation rate (i.e. the value of the rate constant K) decreased with an increased water curing period for the whole range of zero to 28 days water curing. The continued reduction in carbonation rate for curing periods greater than 7 days is in disagreement with Ho and Lewis' observations.

As the two sets of experiments differ through

(a) total age of specimens prior to carbonation
(b) air curing period prior to carbonation

it would seem that these differences and, in particular, (b) might play a significant role in subsequent carbonation rates.

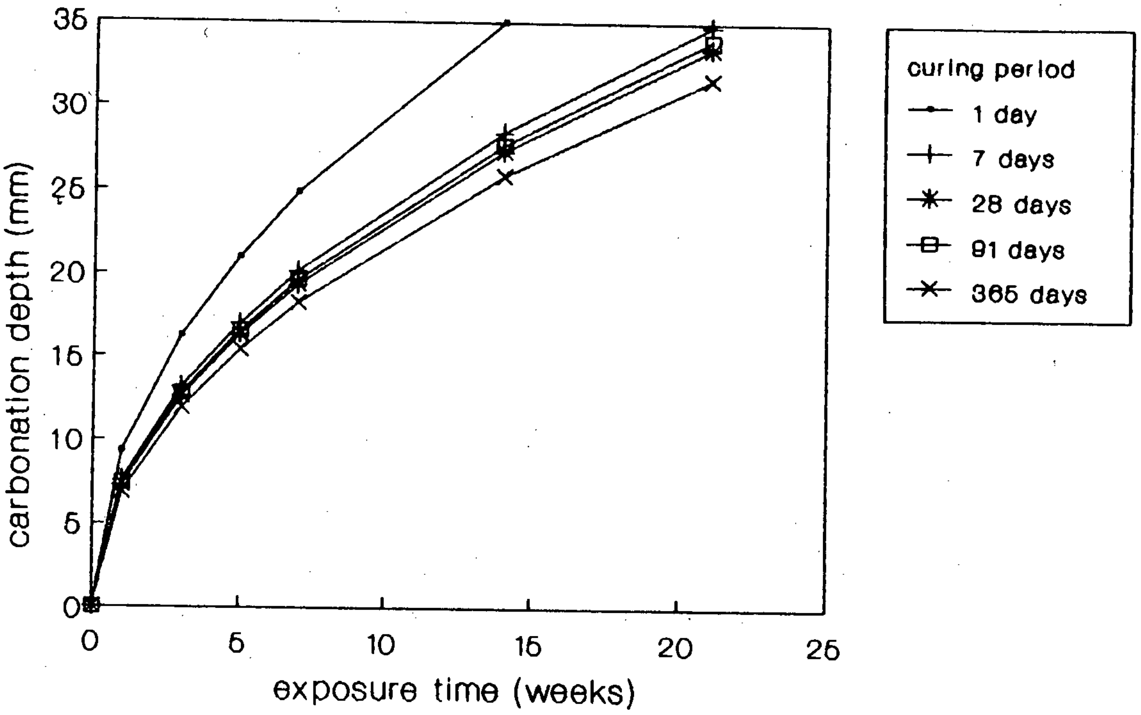
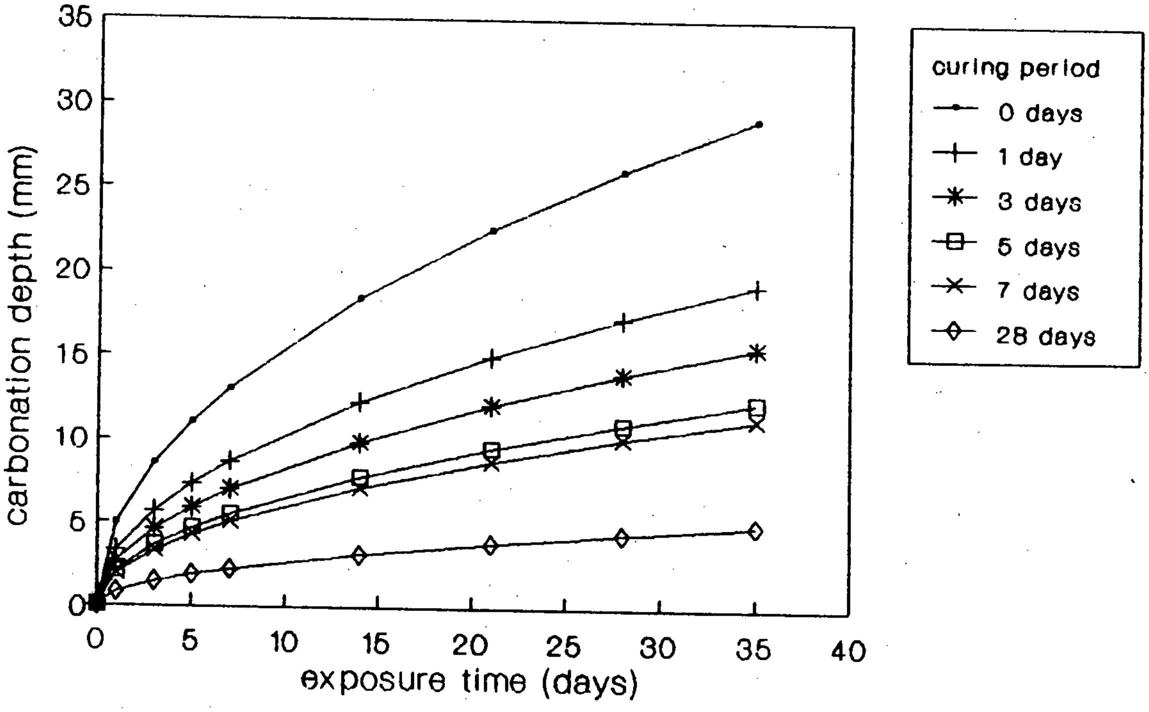


Figure 9.12 : Comparison of carbonation depth with time for varying water curing periods using the carbonation rate constant, K (from Ho and Lewis, 1987).



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SECTION B

CHAPTER 10

EXPERIMENTAL INVESTIGATION INTO THE INFLUENCE OF CURING REGIME ON ACCELERATED CARBONATION

10.1 INTRODUCTION

The literature review in Chapters 9 and 10 on gaseous phase carbonation of cement concrete shows that the curing regime has a profound effect on subsequent accelerated carbonation rates. In this regard, the review reveals that contradicting findings as to the influence of water and subsequent air curing on carbonation rates exist.

In an attempt to clear these contradictions, and determine the influences of both water and air curing, an experimental investigation was undertaken and is reported in this chapter.

10.2 MEASUREMENT OF THE INFLUENCE OF CURING REGIME ON CARBONATION RATES

10.2.1 Theory

Carbonation rates are assessed by measuring the changes in carbonation depth with time. In this investigation these measurements were carried out on cement concrete samples which had undergone a variety of curing regimes prior to exposure to high carbon dioxide partial pressures. Briefly the curing regimes were as follows :

(a) To determine the influence of water curing period on subsequent carbonation rates, six samples were initially exposed to a range of water curing periods varying from 1 to 28 days and thereafter these samples were air cured for 21 days.

(b) To determine the influence of air curing period on subsequent carbonation rates, 6 samples were all initially water cured for the same period of time (14 days) and thereafter exposed to a range of air curing periods varying from 0 to 21 days.

Samples were then placed in a carbonation chamber where they were exposed to an enriched carbon dioxide partial pressure of $\bar{p}\ CO_2 = 0{,}13$ atmospheres. Carbonation depth with time was monitored. The carbonation rates for each sample were modelled by fitting the experimental data to the rate equation, Equation 9.11, Chapter Nine, and the carbonation rate constant, K , determined. An assessment of the quantitative influence on carbonation rate of (a) water curing period and (b) air curing period was then affected. This was achieved by comparing the values determined for the rate constant, K , under the various experimental conditions.

10.2.2 Experimental preparation

(a) Cement concrete mix design

A cement concrete mix design similar to those used in the literature (*inter alia* Fattuhi, 1988 and Ho and Lewis, 1987) was used to give a medium strength concrete with a 28 day strength of approximately 30 MPa. To ensure good compaction it was designed with a slump of 40 mm. The mix design was 2,65 : 2,63 : 1,00 : 0,66 of washed gravel : sand : ordinary Portland cement : water. The aggregates were local Cape Flats dune sand and Malmesbury shale coarse aggregate.

The dune sand typically has very little fines content. The crushed coarse aggregate was 13 mm and flaky in shape.

(b) Cement concrete sample preparation

When preparing a mix, cement, sand and dry aggregate were placed into a mechanical mixer. The mixer was then started and the water slowly added. The freshly mixed concrete was cast into both steel moulds of size 75 x 75 x 300 mm and standard steel 100 mm cube moulds (the former being used for carbonation rate tests and the latter for 28 day compressive strength tests).

To cast the concrete the lightly oiled moulds were placed onto a vibrating table where the concrete was cast in three compacted layers. The exposed face of the sample was trowelled and the samples were then left to set for 24 hours under wet hessian. After this initial 24 hour period the samples were then cured as discussed under experimental procedures, i.e. Section 10.2.3.

(c) Carbonation chamber

An adapted 200 litre epoxy coated metal drum was used for the accelerated carbonation tests (see Figure 10.1). Referring to the figure, samples were placed onto the galvanised wire mesh sample racks (3); carbon dioxide was flushed into the airtight carbonation chamber from the gas bottle (5) by means of an inlet pipe (6); escaping gases left through the outlet pipe (13); gas samples from within the chamber were obtained via the sample part (7) and the carbon dioxide partial pressure was monitored with a calibrated radiometer probe. Temperature and humidity within the carbonation chamber were measured using a Thies temperature and humidity recorder (9) placed within the chamber. A desired relative humidity of between 50 and 75 % was maintained by placing a saturated salt solution of pottasium nitrate (10) in the chamber. In order to achieve sufficient gas movement for the saturated salt solution to be effective in controlling relative humidity, an internal fan (11) was installed. This fan was controlled by a timing device (12) to be on for 30 seconds every 9 minutes. A measured relative humidity of 70 % at a constant temperature of 20°C was maintained.

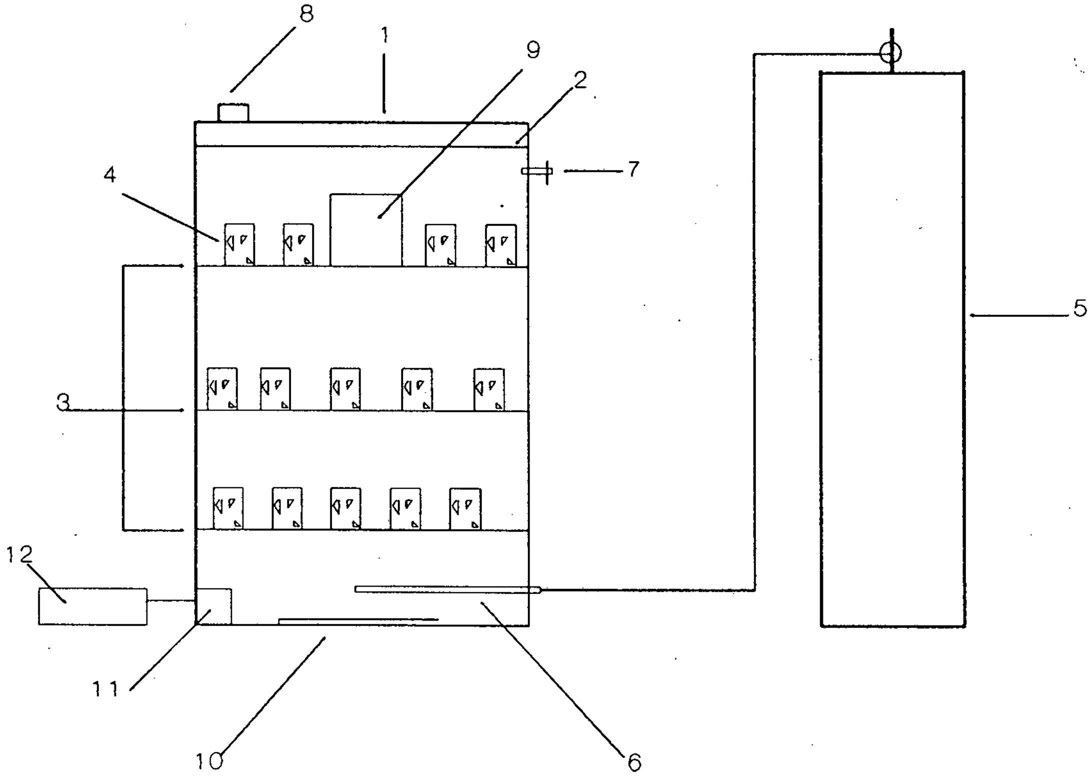


Figure 10.1 : The carbonation chamber used for accelerated carbonation tests (1 = sealed lid, 2 = hessian sack, 3 = sample rack, 4 = cement concrete sample, 5 = 14% CO_2 source, 6 = inlet pipe, 7 = sample port, 8 = airtight stopper, 9 = temperature and humidity recorder, 10 = potassium nitrate solution, 11 = internal fan, 12 = timing device).

10.2.3 Experimental procedure

(a) Curing procedures

After the initial 24 hour period under wet hessian sacking, carbonation rate test samples were cured as follows :

(i) 6 of the 75 x 75 x 300 mm prisms were used to test the influence of water curing on accelerated carbonation rates. These were stripped from their moulds and placed into a 20°C water bath for periods of time varying between 1 and 28 days. Thereafter they were placed in a constant temperature-humidity room at 20°C and 50 % relative humidity for 21 days (see Table 10.1). That is, these samples were subjected to varying initial water curing periods followed by a fixed air curing period.

(ii) Another 6 of the 75 x 75 x 300 mm prisms were used to test the influence of air curing period on accelerated carbonation rates. These were stripped from their moulds and placed into a 20°C water bath for a set period of 14 days. Thereafter they were removed and placed in a constant temperature humidity room at 20°C and 50 % relative humidity for periods of time from 0 to 21 days (see Table 10.2). That is, these samples were subjected to a set initial water curing period followed by a varying air curing period.

The 100 mm cubes were stripped after 24 hours and placed into the water bath for 27 days. These were then tested for 28 day compressive strength as a control check on the mix design.

(b) Carbonation procedure

After the required curing regime samples were carbonated. The samples were placed in the carbonation chamber a minimum distance of 30 mm apart to ensure that adequate carbon dioxide was available to all surfaces. The chamber was flushed with a carbon dioxide/nitrogen gas mix with the required partial pressure of carbon dioxide ($\bar{p}$ CO_2 = 0,13 atmospheres). The carbon dioxide partial pressure within the chamber was closely monitored and maintained within 0,005 atmospheres of the desired 0,13 atmospheres.

(c) Carbonation depth measurement

Depth of carbonation of the samples with time was measured after predetermined periods in the carbonation chamber. Carbonation depth was measured on day 1, 3, 5, 7, 11, 17, 25, 35, 38, 45, 47 and 58 of containment within the carbonation chamber. Depth of carbonation was measured by splitting a sample using a Droxler compressive strength machine and two small steel bars (ϕ = 3 mm) to effectively slice off a 50 mm section. The phenolphthalein test was used to measure the depth of carbonation of this slice.

TABLE 10.1 : Curing regime for Series One tests to determine the influence of water curing on accelerated carbonation rates.

Sample	Water Curing Period (days)	Air Curing Period (days)
1	1	21
2	3	21
3	5	21
4	7	21
5	14	21
6	28	21

TABLE 10.2 : Curing regime for Series Two tests to determine the influence of air curing on accelerated carbonation rates.

Sample	Water Curing Period (days)	Air Curing Period (days)
7	14	0
8	14	1
9	14	3
10	14	7
11	14	14
12	14	21

The phenolphthalein test is carried out by spraying a freshly split surface of the concrete with a mixture of 1 % phenolphthalein (a pH indicator) and 99 % ethenol (Hobbs, 1988). The pH indicator changes from colourless to magenta as the pH rises above about pH 8,3. On a broken concrete surface there is a distinct colour change from reddish purple for non-carbonated high pH conditions to colourless in the carbonated lower pH zone. This is the simplest carbonation depth test and is as accurate as more complicated tests (Ho and Lewis, 1985).

The depth of the carbonated surface layer was measured using a vernier caliper of 0,2 mm accuracy as follows. Referring to Figure 10.2 measurements were taken along the centroidal axes x and y (i.e. along an axis passing through the midpoints of each face of the slice). Where a coarse aggregate particle obstruction occurred along either of these axes, the nearest path to these axes was chosen. The depth of carbonation, d_c in Equation 9.11, was determined as the average of the measured depths on the 4 faces of the slice. All prisms were returned to the chamber after removing the required slice.

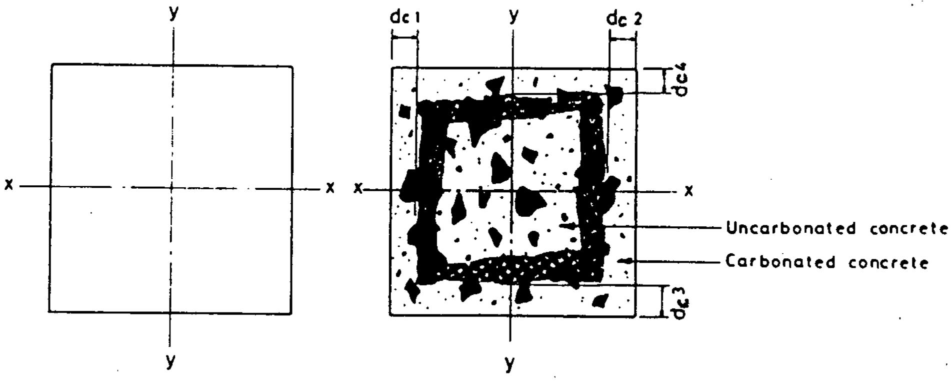


Figure 10.2 : Locations for depth of carbonation (d_c) measurements on freshly broken concrete prisms.

10.3 ANALYSIS OF TEST RESULTS

10.3.1 Introduction

Laboratory scale tests to determine carbonation depth with time (effected to assess the relative influences of water and air curing on subsequent carbonation rates) were carried out as described above in Section 10.2.3. Presentation and analysis of these results is most easily achieved via a graphical approach using the generally accepted carbonation rate equation, Equation 9.11, i.e.

$$d_c = X_o + K t_c^{0,5}$$

where X_o = initial depth of carbonation (mm)
d_c = depth of carbonation (mm)
K = carbonation rate constant
t_c = exposure period (days)

The relative rate of K in the above equation (Equation 9.11) is used to assess relative carbonate rates, the higher the value of K the greater the relative carbonate rate. The rate of K is determined by plotting the depth of carbonation ($d_c - X_o$) against the square root of time to effect such a depth ($t_c^{0,5}$).

A statistical package, Statgraphics, was used to obtain the best fit of observed data to Equation (9.11) via linear regression analysis. An insight into the influence of both water and air curing periods on carbonation rates is then obtained by comparing the rate constants, so determined, for the various curing regimes.

10.3.2 Experimental results

(a) Influence of water curing period on accelerated carbonation rates

Six samples were exposed to 1, 3, 5, 7, 14 and 28 days water curing respectively, followed by 21 days air curing period prior to carbonation (samples 1 to 6 in Table 10.1). These samples, termed the Series One test samples, were then carbonated by exposing them to an enriched carbon dioxide partial pressure of $\bar{p}\ CO_2 = 0,13$ atmospheres. Measurement of carbonation depth with time was taken at regular intervals up to 38 days. In Figures 10.3 to 10.8 are shown plotted the depth of carbonation with square root of time together with the best fit for linearity, the formulated carbonation equation including the 'K' value in Equation 9.11 and a regression analysis of the fit.

(b) Influence of air curing on accelerated carbonation rates

Six samples were exposed to 0, 1, 3, 7, 14 and 21 days air curing respectively prior to carbonation (Samples 7 to 12 in Table 10.2). These samples, termed the Series Two test samples, were then exposed to an enriched carbon dioxide partial pressure as in (a) above. Measurement of carbonation time with depth was taken at regular intervals up till 58 days. In Figures 10.9 to 10.14 are shown the depth of carbonation with square root of time together with the best fit for linearity, the formulated carbonation equation and a regression analysis of the fit.

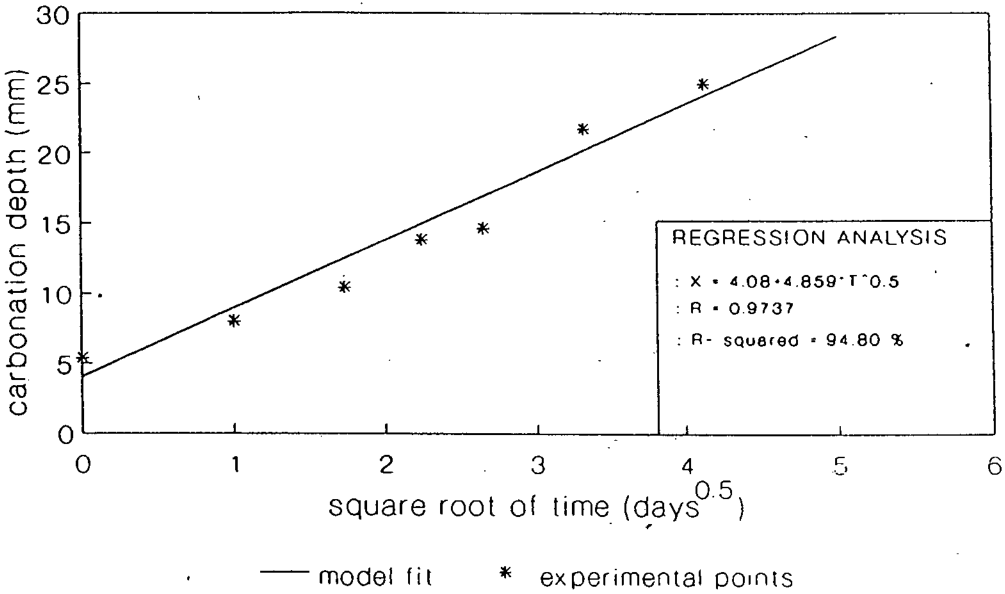


Figure 10.3 : Linear regression fit of measured carbonation depth with square root of time for sample 1 to determine influence of water curing period on carbonation rate.

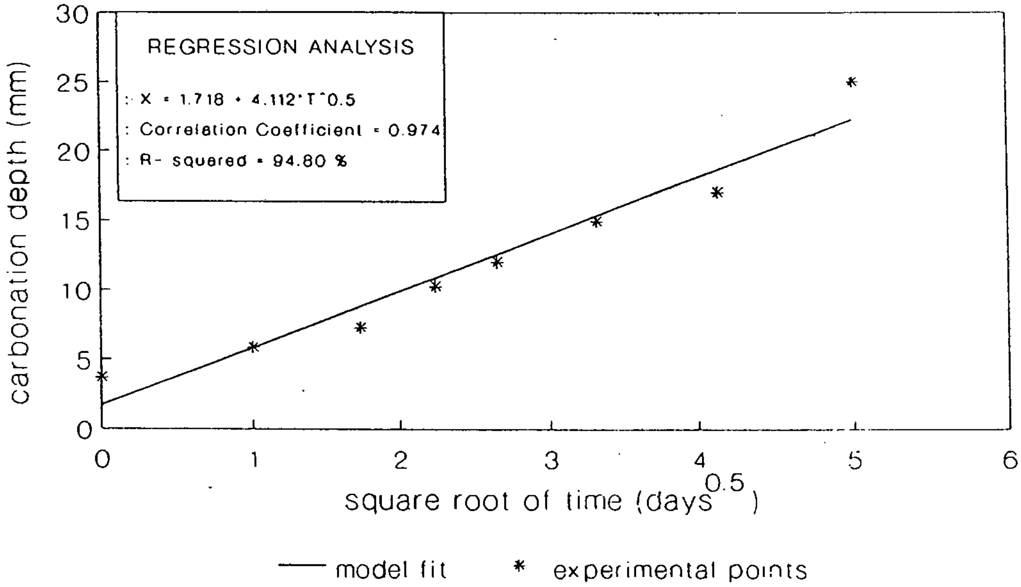
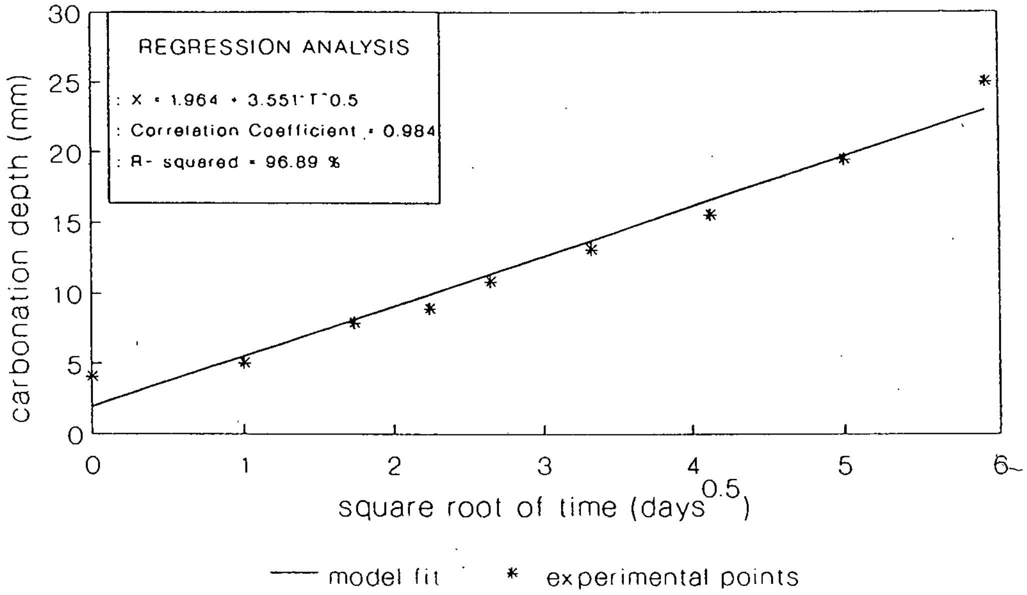


Figure 10.4 : Linear regression fit of measured carbonation depth with



<u>Figure 10.5</u> : Linear regression fit of measured carbonation depth with square root of time for sample 3 to determine influence of water curing period on carbonation rate.

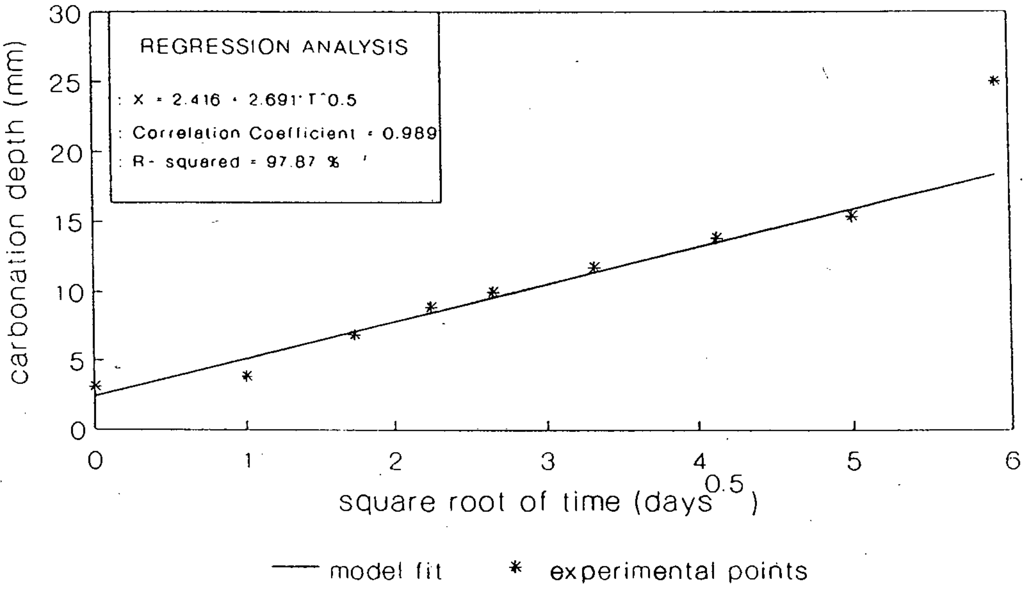


Figure 10.6 : Linear regression fit of measured carbonation depth with

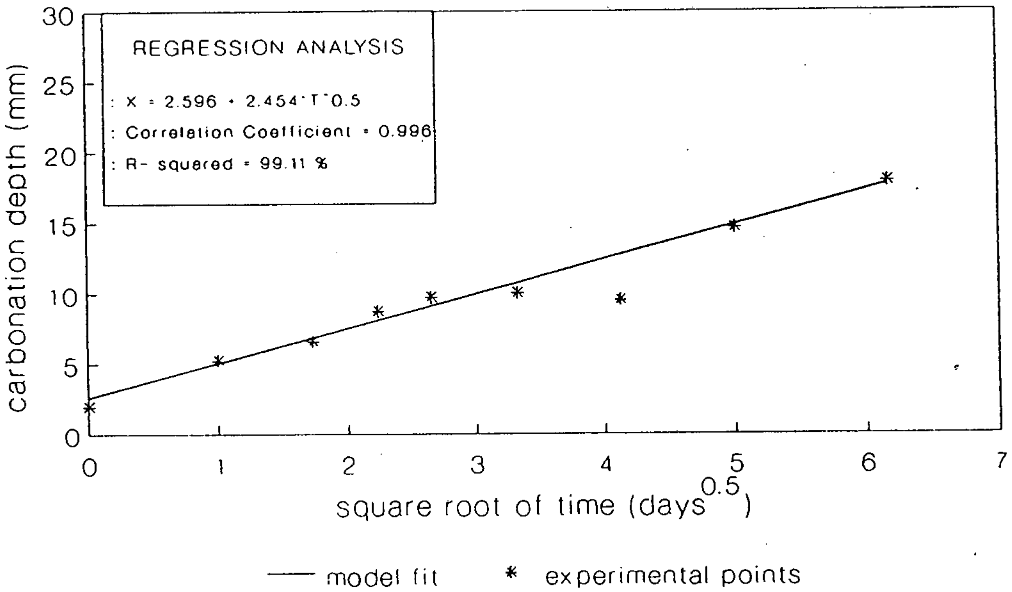


Figure 10.7 : Linear regression fit of measured carbonation depth with square root of time for sample 5 to determine influence of water curing period on carbonation rate.

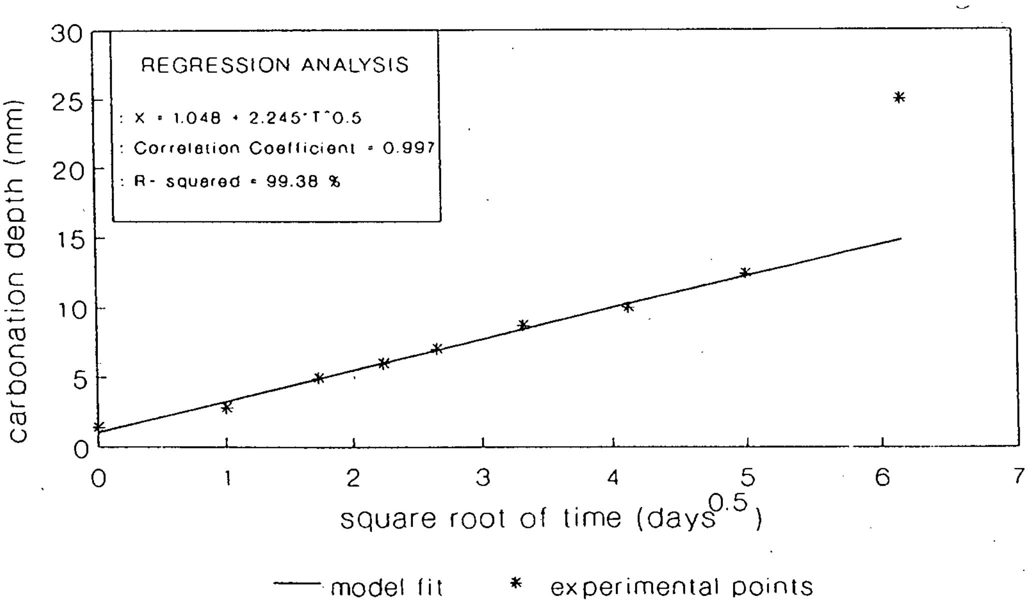


Figure 10.8 : Linear regression fit of measured carbonation depth with

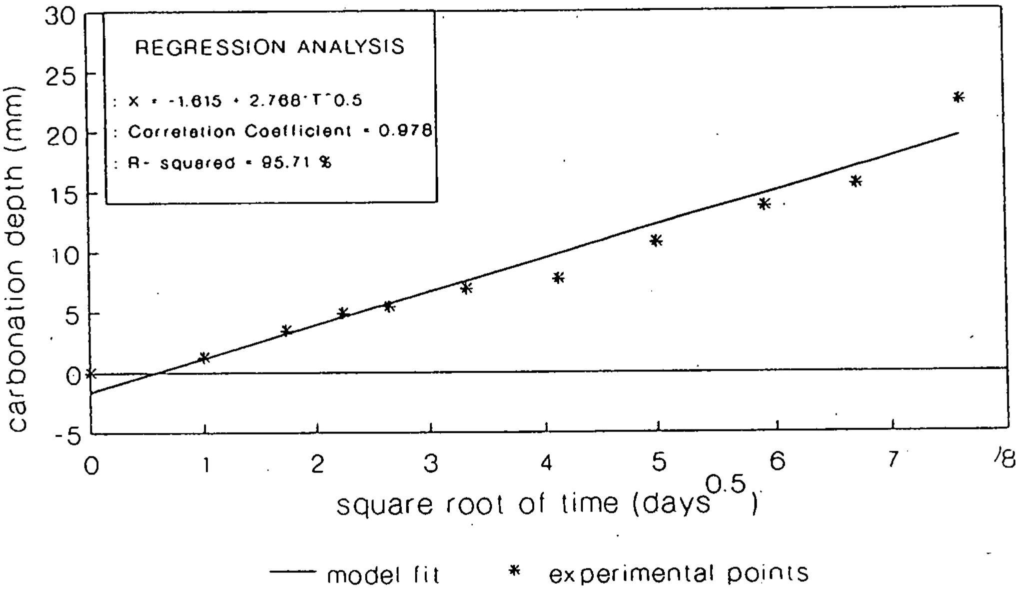


Figure 10.9 : Linear regression fit of measured carbonation depth with square root of time for sample 7 to determine influence of air curing period on carbonation rate.

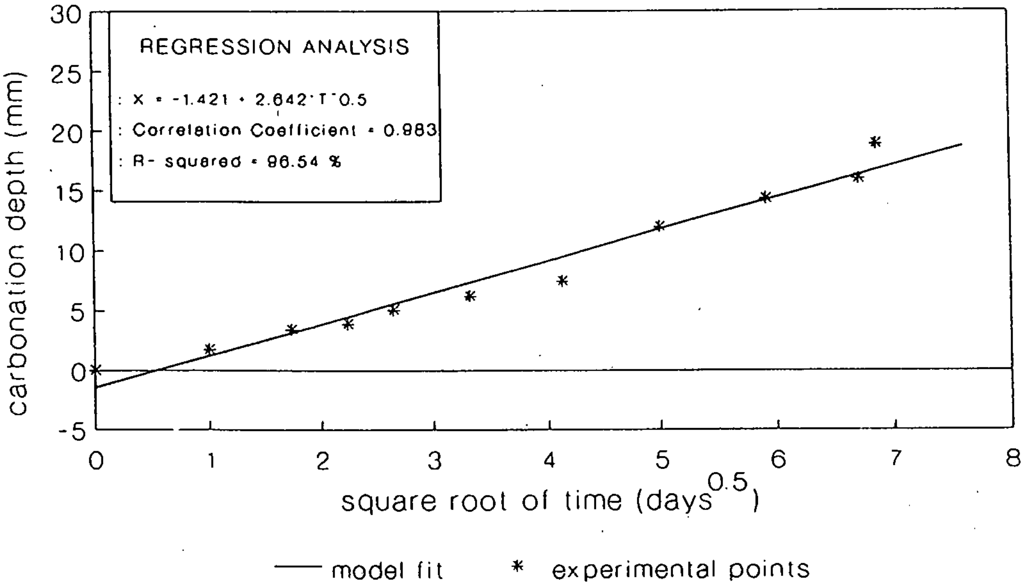


Figure 10.10 : Linear regression fit of measured carbonation depth with square root of time for sample 8 to determine influence

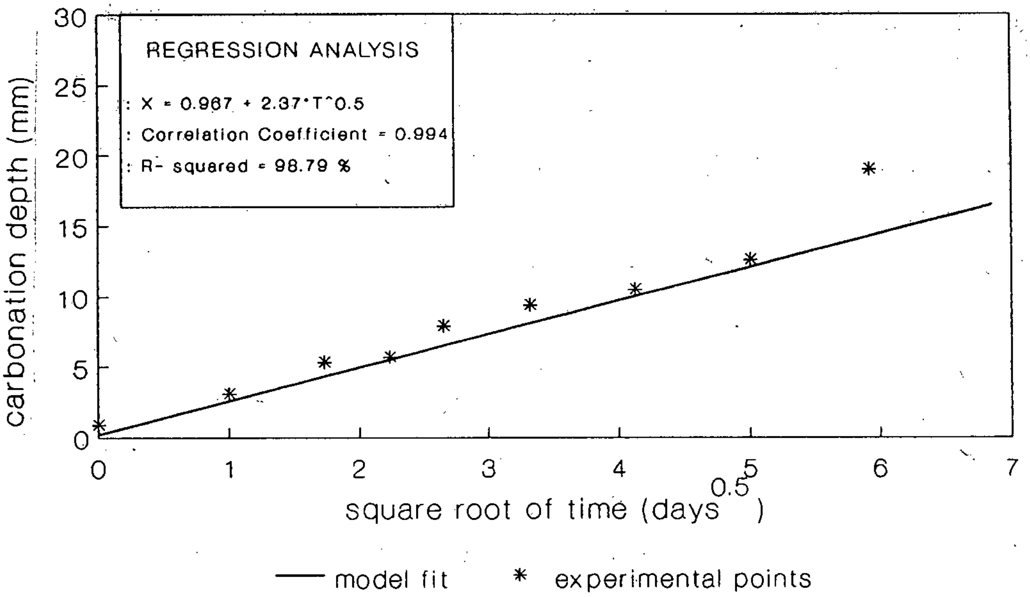


Figure 10.13 : Linear regression fit of measured carbonation depth with square root of time for sample 11 to determine influence of air curing period on carbonation rate.

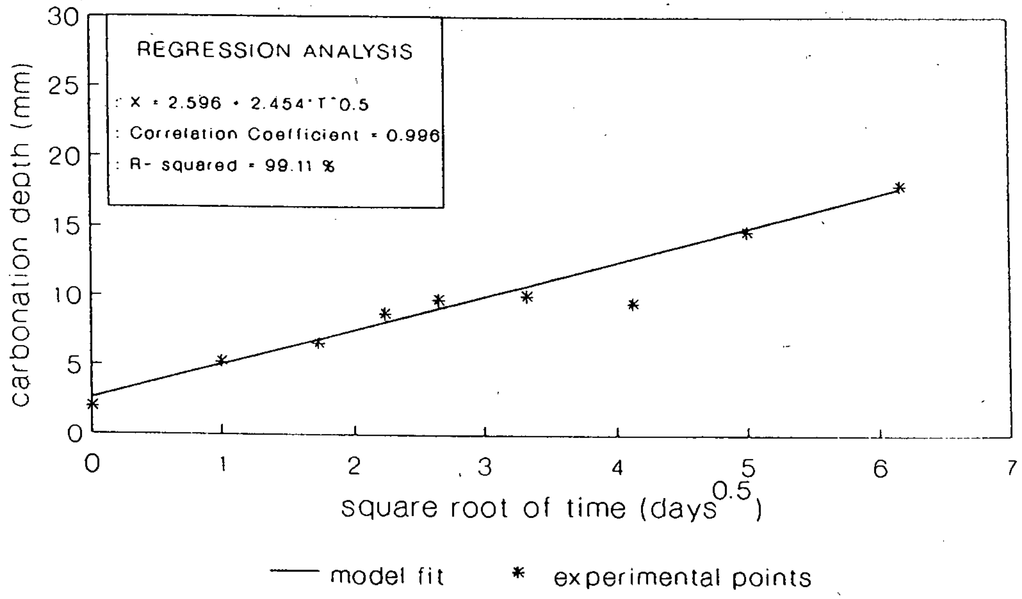


Figure 10.14 : Linear regression fit of measured carbonation depth with

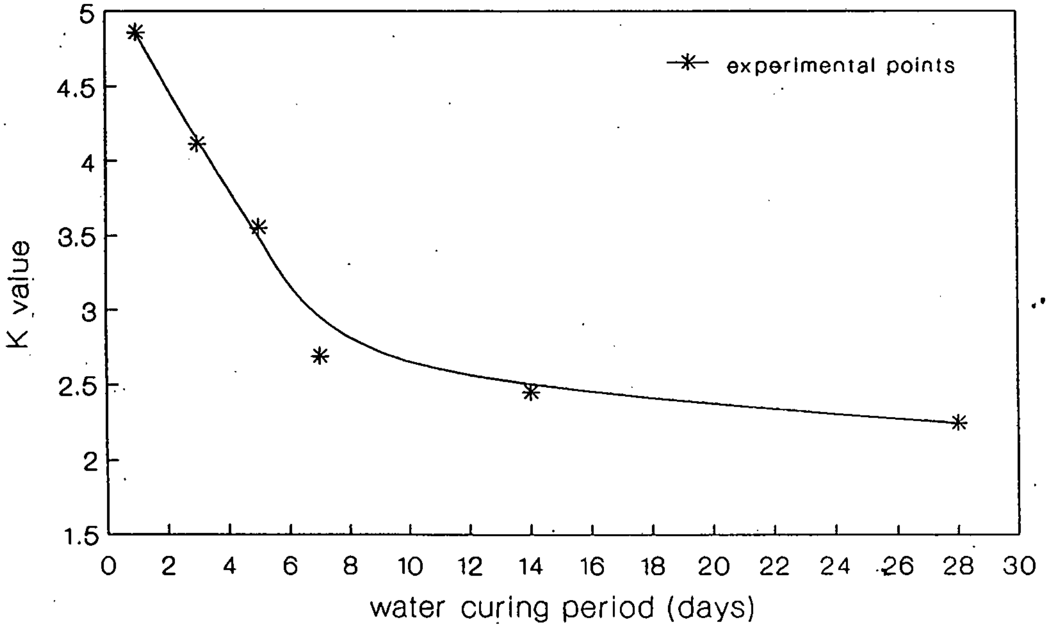
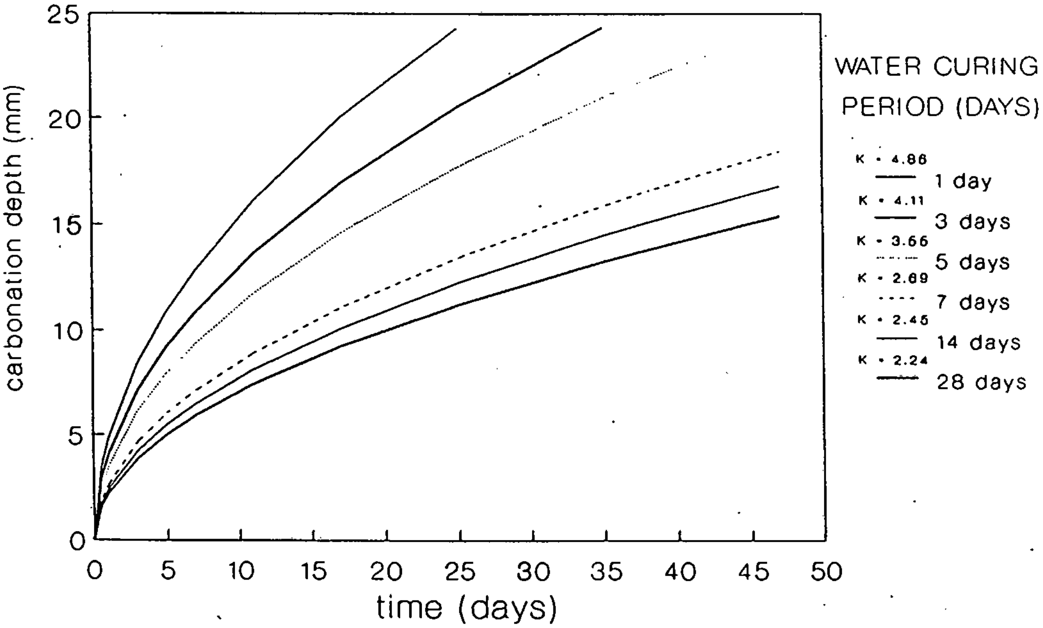


Figure 10.15 : Influence of water curing period on carbonation rate constant, K.



(b) Influence of the air curing period on subsequent carbonation rates

The influence of air curing period on subsequent carbonation rates (for a constant water curing period) is, as in (a) above, assessed in terms of the carbonation rate constants reported in Section 10.3.2 above. A plot of carbonation rate constant versus air curing period the for Series Two test samples is shown in Figure 10.17. From this plot it is apparent that the shorter the air curing period the greater is the subsequent carbonation rate (for a set water curing period). The value of the carbonation rate constant, K, is seen to vary between 2,78 (0 days air curing) and 2,4 (14 days air curing). These differences are not dramatic. The influence occurs principally for air curing periods up to 14 days.

A visual interpretation of the influence of air curing period on carbonation depth with time is shown plotted in Figure 10.18. This plot of carbonation depth with time for samples with varying air curing period is obtained using Equation 9.11 and the K values determined and reported in Section 10.3.2 (for comparative purposes X_o is set to zero). This plot confirms that the influence of air curing period on subsequent carbonation rate is not significant.

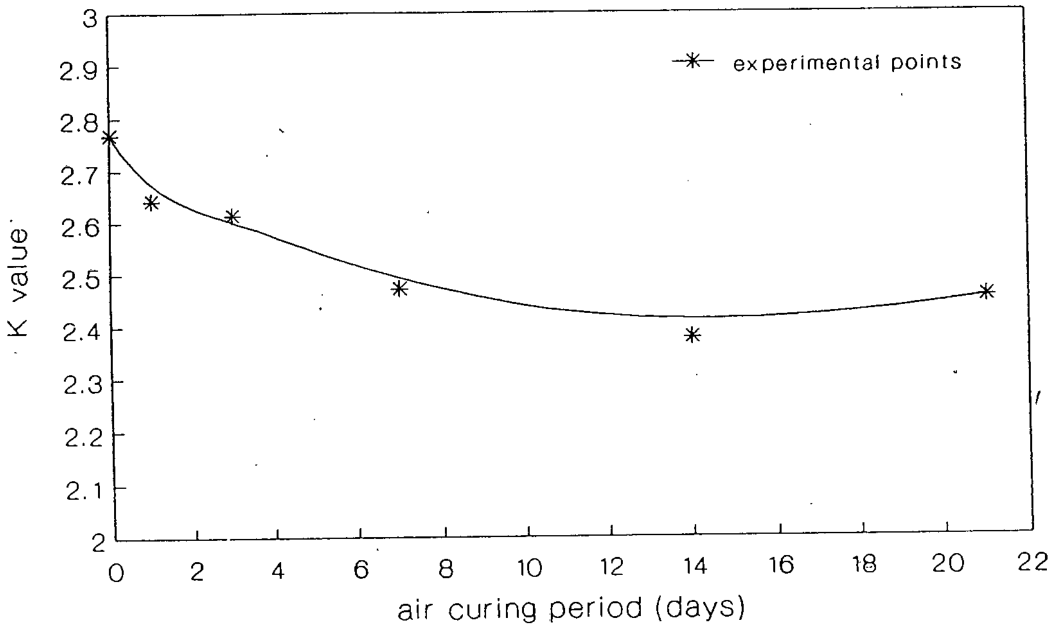
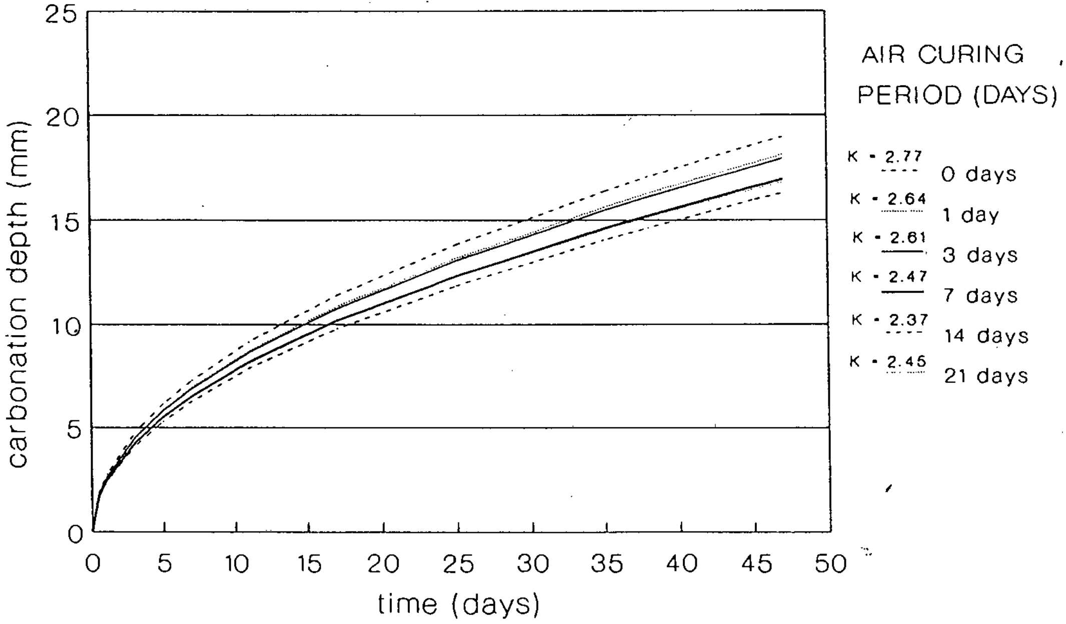


Figure 10.17 : Influence of air curing period on carbonation rate constant, K.



10.3.4 Discussion

Section 10.3.3 above shows that both water curing period and air curing period have an influence on subsequent carbonation rates. The relative effects of each on carbonation rates are now addressed.

(a) Water curing

The observations reported have indicated that carbonation rate decreases significantly with water curing period up to 7 days; further increase in water curing period has negligible effect (see Figure 10.15). (This decrease in carbonation rate is to be expected in terms of the reduction in permeability of cement materials with increasing water curing period (see Section 9.1.1)). These findings are in agreement with data reported by Ho and Lewis (1987) but differ in some respects with the data of Fattuhi (1988). In Figure 10.19 are shown plotted carbonation rate constants, K, versus water curing period for data from the above two investigations and data from this investigation. The plots show particular trends, and it is those trends which are of importance rather than the absolute values. This is because the absolute values can vary significantly with such parameters as partial pressure of carbon dioxide, relative humidity, cement concrete properties etc. The data of Ho and Lewis follows a trend closely similar to that of this investigation, i.e. an initial rapid decrease in carbonation rate constant, K, with water curing period up to 7 days followed by almost no further decrease in carbonation rate constant beyond 7 days water curing. The data of Fattuhi also shows an initial rapid decrease (up to 7 days), however, for periods beyond 7 days a continued reduction in the carbonation rate constant, K, with water curing period is reported. The anomalous findings of Fattuhi are difficult to explain. However, the one significant difference between Fattuhi's experimental procedure and that of Ho and Lewis and this investigation is that Fattuhi also varied air curing period with water curing period whereas the former investigations did not. Fattuhi varied air curing period in a consistent fashion whereby a <u>total curing period of 28 days</u> was used, i.e. as water curing period increased air curing period decreased. Taking cognisance of the above it was deemed important to investigate air curing period *per se* influences carbonation rate.

(b) Air curing

The influence of air curing period (with constant water curing period of 14 days) on carbonation rate constant, K, is shown in Figure 10.17. Following a similar trend to the effects of water curing period, the longer the air curing period the lower the subsequent carbonation rates. However, the influence are not as pronounced as those for water curing. This is indicated in Figure 10.20 which shows a decrease in carbonation rate over 21 days of only about 13% with varying air curing period compared with about 50% for a similar water curing period. Nevertheless, the fact that air curing period also influences subsequent carbonation rates highlights the importance of maintaining constant air curing period when investigating influence of water curing period. It is likely therefore that the difference in observation of the influence of water curing period on carbonation rates between Fattuhi and those of Ho and Lewis and this investigation are as a result of Fattuhi's use of a constant total curing period. This approach results in significant variance in air curing period as water curing period was varied from 1 to 28 days.

No attempt to adjust Fattuhi's data using the results of this investigation for influence of air curing period can be made as the influence of air curing on carbonation rates investigated here were only carried out for one water curing period, that of 14 days. Ideally investigations for other constant water curing periods should have been implemented.

In conclusion the following can be stated :

(a) Carbonation rate decreases with increasing water curing period for a particular constant air curing period. The rate decreases significantly with a water cruing period up to 7 days; further increase in water curing period has negligible influence.

(b) Carbonation rate decreases with increasing air curing period for a particular constant water curing period (prior to air curing). However, the influence of air curing period on carbonation rates is significantly less than that of water curing period (i.e. (a) above).

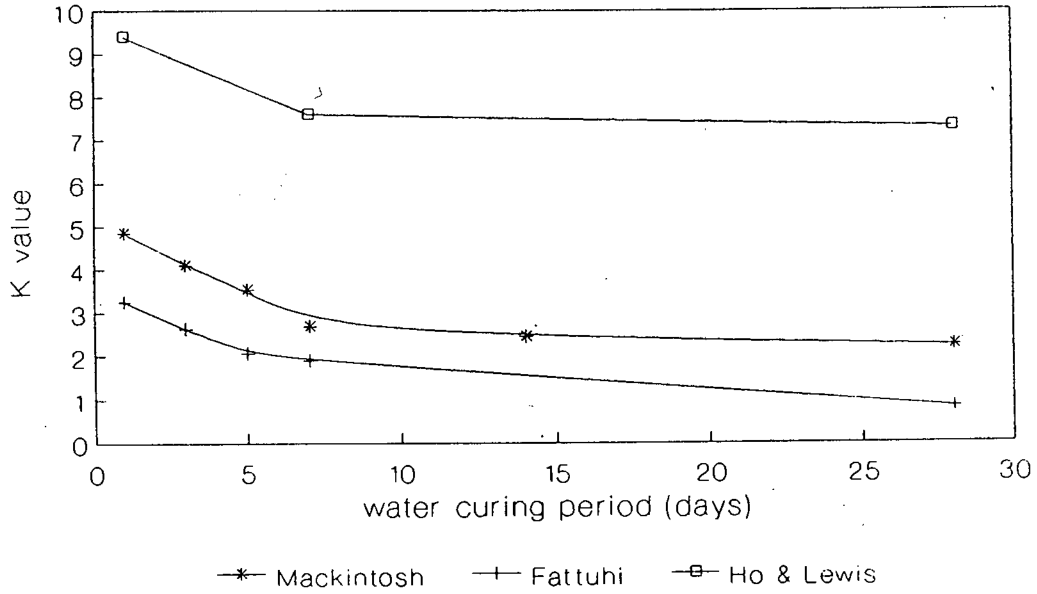
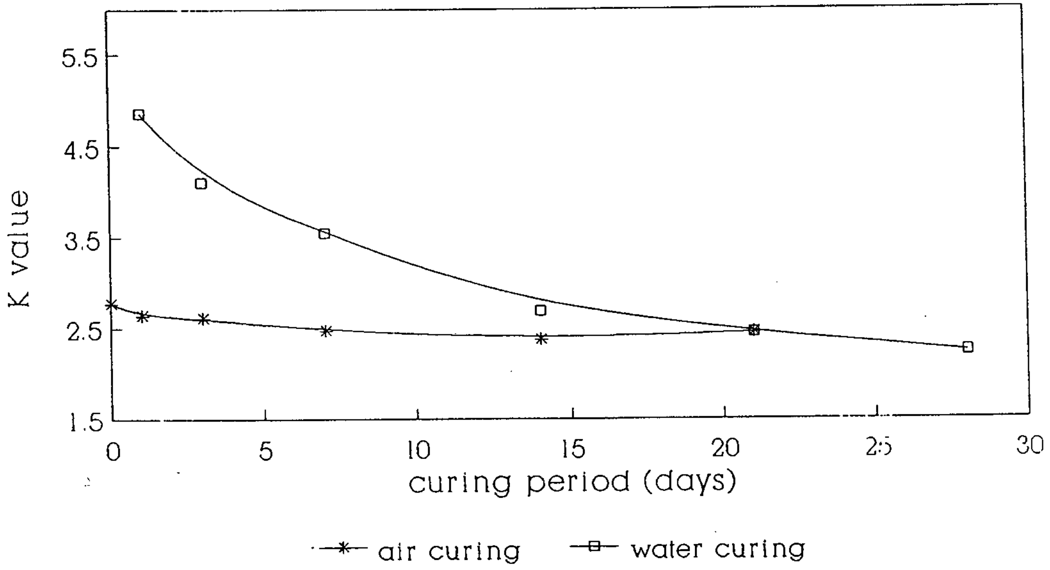


Figure 10.19 : Comparison of the influence of water curing period on carbonation rate constant, K, using data from this investigation, Ho and Lewis (1987) and Fattuhi (1988).



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SECTION B

CHAPTER 11

GENERAL CONCLUSIONS

11.1 CONCLUSIONS

The principal objective of this section of the investigation was an enquiry into the influence of curing regime on subsequent accelerated carbonation rates - the purpose being to provide further information on the practical implementation of accelerated carbonation to reduce the rate of attack by aggressive water on cement concrete. This was carried out using a laboratory scale experimental investigation.

In the experimental investigation, detailed in Chapter 11, carbonation was effected by exposing cement concrete samples to an enriched carbon dioxide partial pressure in a carbonation chamber. Carbonation depth with time was monitored enabling carbonation rates to be determined. From these studies it was possible to assess the influence on carbonation rate of both water curing period (with a single fixed air curing period) and air curing period (with a single fixed water curing period). These observations revealed the following :

(a) Both water curing period and air curing period influence subsequent carbonation rates, but the influence of the latter is considerably less than that of the former.

(b) With regard to the influence of water curing period :

  (i) Water curing period has a significant influence on subsequent accelerated carbonation rates - the carbonation rate for cement concrete water cured for 28 days being approximately 50% of the carbonation rate for cement concrete water cured for 1 day.

(ii) The influence of water curing period on subsequent accelerated carbonation is most pronounced up to 7 days; further increase in water curing period has negligible influence on subsequent carbonation rates. This finding is in agreement with that of Ho and Lewis (1987).

(c) With regard to the influence of air curing period :

(i) Air curing period has a small but measurable influence on subsequent accelerated carbonation rates - the carbonation rate for cement concrete cured for 21 days being approximately 13% of the carbonation rate for cement concrete cured for zero days.

(ii) The influence of air curing period on subsequent carbonation rates is most pronounced up to 7 days; further increase in air curing period results in negligible decrease in subsequent carbonation rates.

(d) The observations regarding the influence of water curing period on subsequent carbonation, i.e. (b) above, and the influence of air curing period on subsequent carbonation, i.e. (c) above, are both for single air curing and water curing periods respectively. These observations therefore cannot be regarded as general until tested for a range of air curing periods and water curing periods respectively. It is recommended that this aspect be given attention in future research into cement concrete accelerated carbonation.

The experimental findings reported here indicate that creation of a protective calcium carbonate layer on cement concrete can be readily attained via accelerated carbonation. Furthermore, the findings indicate that the period required to effect such a carbonated layer is significantly influenced by curing regime prior to carbonation, and this aspect should be taken into account when considering the practical implementation of accelerated carbonation.

APPENDIX A

CALCULATION OF ACTIVITY COEFFICIENTS WITH THE AID OF THE DAVIES EQUATION

In low salinity water (TDS $\leq$ 2 500 mg/ℓ) activity coefficients of ions can be determined from the Debye-Huckel theory or some modification of it. The most widely used modification of this theory is that by Davies (Loewenthal *et al* 1986)[1], viz. :

$$\log f_1 = -AZ_i^2\left(\frac{\mu^{1/2}}{1+\mu^{1/2}} - 0,3\,\mu\right) \qquad (A.1)$$

where f_i = activity coefficient for ionic species i, written as f_m and f_d for mono and divalent ions respectively

μ = ionic strength

= $\frac{1}{2}\,\Sigma\, C_1\, Z_i^2$

C_1 = concentration of the i^{th} ionic species, mol/ℓ

Z_i = charge of the i^{th} species, equal to 1 for mono and 2 for divalent ions

A = temperature dependant constant

= $1,825.10^6\ (78,3.T)^{-1,5}$

= 0,504 at 25°C

T = temperature in Kelvin.

To calculate the ionic strenth, μ , requires a complete analysis of the water. However, the activity coefficients determined from the Davies equation are not very sensitive to ionic strength so that an approximate estimate of μ from empirical methods is usually sufficient. Two empirical equations are available (Kemp, 1971), i.e.

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[1] Loewenthal, R.E., Wiechers, H.N.S. and Marais, G.v.R. (1986), "Softening and stabilization of municipal waters". Published by the

- $\mu \approx 2{,}5.10^{-5}.(\mathrm{TDS} - 20)$

where TDS = total inorganic dissolved solids, mg/ℓ.

- $\mu = 1{,}68.10^{-4}.\mathrm{SC}$

where SC = specific conductance, in mS/m.
(1 mS/m = 10 μ mho/cm)

Example : Determine momovalent and divalent activity coefficients for water with ionic strength $\mu = 0{,}010$. For this ionic strength, the monovalent ion activity coefficient f_m at 25°C is :

$$\log f_m = -0{,}504(1)^2 \{0{,}010^{½}/(1 + 0{,}010^{½}) - 0{,}3.0{,}010\}$$
$$= -0{,}0443$$

Hence $f_m = 10^{-0{,}0443}$
$= 0{,}903$

and the divalent ion activity coefficient f_d is

$$\log f_d = -0{,}504(2)^2 \{0{,}010^{½}/(1 + 0{,}010^{½}) - 0{,}3.0{,}010\}$$
$$= -0{,}1772$$

Hence $f_d = 10^{-0{,}1772}$
$= 0{,}665$.

APPENDIX B

MEASUREMENT OF ALKALINITY AND ACIDITY USING GRAN FUNCTIONS

B.1 FORMULATION OF GRAN FUNCTIONS

In the measurement of alkalinity and acidity as outlined in Section 4.2 it is necessary to determine the equivalence point and to titrate to that pH as an endpoint. To bypass the difficulty of identifying the endpoint pH, Gran (1952)[1] proposed the use of titration functions. Gran showed that in the pH region above and below an equivalence point there is a region in which various expressions formulated by him plot linearly with respect to the volume of standard strong acid added. Two such functions can be formulated for each equivalence point. If the linear portion of each plot is extrapolated to a function value of zero the corresponding value of acid or base added equals the volume to titrate to the equivalence point to give the alkalinity or acidity initially present in the sample.

For the carbonate system six functions can be developed for the three equivalence points. However, these associated with the CO_3^{2-} equivalence point are of little value principally for the following three reasons: first, the titration is carried out in the high pH region where significant ion pairing occurs between OH^- and the cations Ca^{2+} and Mg^{2+} ; if a significant degree of such ion pairing occurs, it is no longer possible to develop a simple Gran function in terms of pH and the incremental addition of strong acid (or base). Second, the possibility of hydroxide mineral precipitation is ever present; should such precipitation occur it will affect the accuracy of the titration. Finally, at the high pH values (necessarily encountered in this titration), carbon dioxide absorption from the air introduces serious errors. For these reasons only those Gran functions associated with the $H_2CO_3^*$ and HCO_3^- equivalence points will be considered.

The Gran functions for alkalimetric and acidimetric titrations of an aqueous solution containing only the carbonate weak acid-base system are developed as follows : Let

V_I = initial volume of sample, mℓ
v_x = volume of standard strong acid added, mℓ
$v_{CO_2}, v_{HCO_3^-}$ = volume of standard strong acid required to titrate the sample to the $H_2CO_3^*$ or HCO_3^- equivalence points respectively
$\bar{C}_a$ = molarity of standard strong acid
Subscript 'x' = value of a particular parameter <u>after</u> adding v_x mℓ of standard strong acid
Subscript 'i' = initial value of a particular parameter, i.e. just before the titration is started.

(a) <u>Gran functions for determining $H_2CO_3^*$ alkalinity</u> (Alkalinity)

(i) Function for the titration in the pH region below the $H_2CO_3^*$ equivalence point :
After adding v_x mℓ standard strong acid, in the region $3 < pH_x < 4$ two expressions can be written down for the Alk_x. First, in terms of the volume of standard strong acid added,

$$Alk_x = \frac{(v_{CO_2} - v_x)\,\bar{C}_a}{V_I + v_x} \qquad (B.1)$$

Second, in terms of species concentrations; in the pH region below $H_2CO_3^*$ equivalence point $[H^+]_x >> [HCO_3^-]_x$ and $[OH^-]_x$ is negligible, so that Equation (4.11) approximates to

$$Alk_x = -[H^+]_x \qquad (B.2)$$

Substituting for Alk_x from Equation (B.2) into Equation (B.1) and cross multiplying

$$[H^+]_x \, (V_I + v_x) = (v_x - v_{CO_2}) \, \bar{C}_a$$

and multiplying both sides of this equation by the activity coefficient for H^+, f_H,

$$(H^+)_x \, (V_I + v_x) = (v_x - v_{CO_2}) \, \bar{C}_a . f_H \qquad (B.3)$$

where $(H^+)_x$ = activity of H^+.

The left and right hand sides of this equation each define the first Gran function, F_{1x}, i.e.

$$F_{1x} = 10^{-pH_x}(V_I + v_x) \qquad (B.4a)$$

and

$$F_{1x} = (v_x - v_{CO_2}) \, \bar{C}_a . f_H \qquad (B.4b)$$

Substituting correspondiong measured values for v_x and pH_x into Equation (B.4a) gives a series of values for F_{1x} ; a plot of F_{1x} versus v_x constitutes the first Gran titration plot. The plot will be linear with slope $(\bar{C}_a f_H)$, this is indicated by differentiating Equation (B.4b) with respect to v_x . Furthermore, from Equation (B.4b), F_{1x} is zero where $v_x = v_{CO_2}$ so that a linear extrapolation of the plot gives v_{CO_2} where the plot intersects the v_x ordinate for $F_{1x} = 0$.

The right and left hand sides of this equation each define the second Gran function, i.e.

$$F_{2x} = 10^{ph_x} (v_{HCO_3} - v_x) \qquad (B.7a)$$

and

$$F_{2x} = \frac{1}{K_1'} (v_{CO_2} - v_x) \qquad (B.7b)$$

Taking Equation (B.7b) and differentiating with respect to v_x, indicates a linear plot for v_x versus f_{2x}; also, linear extrapolation of the plot to $F_{2x} = 0$ gives $v_x = v_{CO_2}$, from which Alkalinity can be determined, i.e.

$$H_2CO_3^* \text{ alkalinity} = v_{CO_2} . \bar{C}_a / V_I$$

Referring to Equation (B.7a), the value of v_{HCO_3} is not determined from the data so far, but is determined from the HCO_3^- alkalinity titration below. Once the value for $vHCO_3$ is known, and inserted in Equation (B.7a) it serves as a check on the value for v_{CO_2} determined in a(i) above.

(b) Gran functions for determining HCO_3^- alkalinity

(i) Function for the titration in the pH region below the HCO_3^- equivalence point, i.e. $6 \leq pH \leq 7$: The Gran function F_{3x} for determining the HCO_3^- alkalinity is formulated in a fashion similar so that for F_{2x} for HCO_3^- alkalinity in section (a)(ii) above, except that whereas in the previous example it was assumed that v_{HCO_3} is known, here it is assumed that v_{CO_2} is known, i.e. from Equations (B.7a and B.7b)

$$F_{3x} = 10^{-pH_x}(v_{CO_2} - v_x) \tag{B.8a}$$

and

$$F_{3x} = K_1'(v_{HCO_3} - v_x) \tag{B.8b}$$

Provided v_{CO_2} is known (or has been determined) it is possible to determine v_{HCO_3} (and hence the HCO_3^- alkalinity) as follows: values for F_{3x} are determined by substituting corresponding observed data for pH_x and v_x into Equation (B.8a). Differentiating Equation (B.8b) with respect to v_x indicates a linear plot for v_x versus F_{3x} with slope $- K_1'$, also, from Equation (B.8b) linear extrapolation of the plot to $F_{3x} = 0$ gives $v_{HCO_3} = v_x$. HCO_3^- alkalinity is then determined as

$$HCO_3^- \text{ alkalinity} = v_{HCO_3} . \bar{C}_a / V_I$$

(ii) Function for the titration in the pH region above the HCO_3^- equivalence point, i.e. $9 \leq pH \leq 9{,}5$: As a check on the HCO_3^- alkalinity value determined in Section (b)(i) above, a fourth Gran function can be developed in the pH region above the HCO_3^- equivalence point. As in Section (a)(ii) above, two equations can be written for each HCO_3^- alkalinity and CO_3^{2-} alkalinity : For HCO_3^- alkalinity, in the pH region of interest $[HCO_3^-]_x$ and $[CO_3^{2-}]_x$ contribute significantly to this alkalinity, whereas both $[H^+]_x$ and $[OH^-]_x$ are negligible, i.e.

$$Alk_x = \frac{(v_{CO_2} - v_x)\bar{C}_a}{V_I + v_x} \cong [HCO_3^-]_x + 2[CO_3^{2-}]_x \tag{B.9}$$

For HCO_3^- alkalinity, the values for $[H^+]_x$, $[OH^-]_x$ and $[H_2CO_3^*]_{a}x$ are all negligible compared with $[CO_3^{2-}]_x$, i.e.

$$HCO_3^- \text{ alk}_x = \frac{(v_{HCO_3} - v_x)}{V_I + v_x} \bar{C}_a = [CO_3^{2-}]_x \qquad (B.10)$$

Dividing Equation (B.9) by Equation (B.10), substituting for $[HCO_3^-]_x/[CO_3^{2-}]_x$ from Equation (4.10) and rearranging terms gives

$$10^{pH_x} (v_{CO_2} - 2v_{HCO_3} + v_x) = \frac{1}{K_2'} (v_{HCO_3} - v_x)$$

The left and right hand sides of this equation each define the fourth Gran function, F_{4x}, i.e.

$$F_{4x} = 10^{pH_x} (v_{CO_2} - 2v_{HCO_3} + v_x) \qquad (B.11a)$$

and

$$F_{4x} = \frac{1}{K_2'} (v_{HCO_3} - v_x) \qquad (B.11b)$$

Substituting values for v_{CO_2} and v_{HCO_3} determined from Subsections (a)(ii) and (b)(i) respectively above into Equation (B.11a), and also for observed data for corresponding values of pH_x and v_x gives a series of values of F_{4x} versus v_x. A plot of F_{4x} versus v_x indicates that the plot will be linear with slope $1/K_2'$, and, linear extrapolation of this plot to F_{4x} equal to zero gives $v_{HCO_3} = v_x$.

B.2 UTILIZATION OF GRAN FUNCTIONS

The Gran functions developed in the previous section are used to determine $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity from data for the alkalimetric (or acidimetric) titration of a water sample in the following steps :

(a) Determination of Alkalinity ($H_2CO_3^*$ alkalinity) from titration data in the region $3 < pH < 3,8$

(i) Calculate a series of values for the first Gran function, F_{1x} , by substituting corresponding values for pH , pH_x , and the volume of strong acid added, v_x , into Equation (B.4a).

(ii) Plot F_{1x} versus v_x ; the plot should be linear in the region $pH \leq 3,8$.

(iii) Extrapolate the straight line section of the plot to intersect the v_x ordinate at $F_{1x} = 0$; the intercept value for v_x gives the volume of strong acid to the $H_2CO_3^*$ equivalence point, v_{CO_2} .

(iv) Determine $H_2CO_3^*$ alkalinity as

$$\text{Alkalinity} = v_{CO_2} . \bar{C}_a / V_I$$

where V_I = initial volume of sample

$\bar{C}_a$ = molarity of H^+ in the standard strong acid.

(b) Determination of HCO_3^- alkalinity from titration data in the region $6 < pH < 7$

(i) Calculate a series of values for the third Gran function, F_{3x} , using the value for v_{CO_2} determined in (a) above and substituting corresponding values for pH , pH_x , and the volume of strong acid added, v_x , into Equation (B.8a).

(ii) Plot F_{3x} versus v_x ; the plot should be linear in the region $6 < pH < 7$.

$$F_{4x} = 10^{pH_x} (v_{CO_2} - 2v_{HCO_3} + v_x) \qquad (B.11a)$$

and

$$F_{4x} = \frac{1}{K_2'} (v_{HCO_3} - v_x) \qquad (B.11b)$$

Substituting values for v_{CO_2} and v_{HCO_3} determined from Subsections (a)(ii) and (b)(i) respectively above into Equation (B.11a), and also for observed data for corresponding values of pH_x and v_x gives a series of values of F_{4x} versus v_x . A plot of F_{4x} versus v_x constitutes the fourth Gran titration.
Differentiating Equation (B.11b) with respect to v_x indicates that the plot will be linear with slope $1/K_2'$, and, linear extrapolation of this plot to F_{4x} equal to zero gives $v_{HCO_3} = v_x$.

The Gran functions developed in the previous section are used to determine $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity from data for the alkalimetric (or acidimetric) titration of a water sample in the following steps :

(a) Determination of Alkalinity ($H_2CO_3^*$ alkalinity) from titration data in the region $3 < pH < 3,8$

(i) Calculate a series of values for the first Gran function, F_{1x} , by substituting corresponding values for pH , pH_x , and the volume of strong acid added, v_x , into Equation (B.4a)

(ii) Plot F_{1x} versus v_x ; the plot should be linear in the region $pH \leq 3,8$.

(iii) Extrapolate the straight line section of the plot to intersect the v_x ordinate at $F_{1x} = 0$; the intercept value for v_x gives the volume of strong acid to the $H_2CO_3^*$ equivalence point, v_{CO_2} .

(iv) Determine $H_2CO_3^-$ alkalinity as

$$\text{Alkalinity} = v_{CO_2}.\bar{C}_a/V_I$$

where V_I = initial volume of sample

$\bar{C}_a$ = molarity of H^+ in the standard strong acid.

(b) Determination of HCO_3^- alkalinity from titration data in the region $6 < pH < 7$

(i) Calculate a series of values for the third Gran function, F_{3x}, using the value for v_{CO_2} determined in (a) above and substituting corresponding values for pH, pH_x, and the volume of strong acid added, v_x, into Equation (B.8a).

(ii) Plot F_{3x} versus v_x; the plot should be linear in the region $6 < pH < 7$.

(iii) Extrapolate the straight line section of the plot to intersect the v_x ordinate at $F_{3x} = 0$; the intercept value for v_x gives the volume of strong acid to the HCO_3^- equivalence point, v_{HCO_3}.

(iv) Determine HCO_3^- alkalinity as

$$HCO_3^- \text{ alk} = \frac{v_{HCO_3}.\bar{C}_a}{V_I}$$

(c) Check on the Alkalinity value using the second Gran function and titration data in the region $6 < pH < 7$

(i) Calculate a series of values for the second Gran function, F_{2x}, using the value for v_{HCO_3} determined in (b) above and substituting corresponding values for pH , pH_x , and the volume of strong acid added, v_x , into Equation (B.6a).

(ii) Plot F_{x2} versus v_x ; the plot should be linear in the region $6 < pH < 7$.

(iii) Extrapolate the straight line section of the plot to intersect the v_x ordinate at $F_{2x} = 0$. The intercept value for v_x gives the volume of strong acid to the $H_2CO_3^*$ equivalence point, v_{CO_3} .

(iv) Determine Alkalinity as

$$\text{Alkalinity} = v_{CO_2} . \bar{C}_a / V_I \ .$$

APPENDIX C

CHEMICAL ANALYSIS OF RAW BROWN WATER FROM KLOOFNEK WATER TREATMENT PLANT

CITY OF CAPE TOWN

City Engineer's Department

Scientific Services Bran

CERTIFICATE OF ANALYSIS

Kloof Nek Raw Water

CB4/K2

October 1988

Weekly Composites

		1988-10-05	1988-10-11	1988-10-18	1988-10-25	-
PHYSICAL						
Conductivity @ 20 C	mS/m	7.8	6.8	8.2	6.4	-
pH		4.98	4.44	5.04	4.42	-
Turbidity	NTU	1.46	1.69	1.39	1.70	-
Colour	Plat.Std	200	200	200	200	-
UV.Absorbance	300nm/40mm	2.142	2.178	2.338	2.164	-
ORGANIC						
PV4 @ 27 C	O mg/l	17.2	17.5	18.7	17.3	-
HARDNESS						
Total	CaCO3 mg/l	9.0	7.5	8.6	8.5	-
MINERAL						
Alkalinity	CaCO3 mg/l	0.0	0.0	1.0	0.0	-
Chloride	Cl mg/l	16.0	16.0	18.0	17.0	-
Sulphate	SO4 mg/l	3.1	3.0	2.9	3.1	-
Calcium	Ca mg/l	1.75	1.24	1.78	1.35	-
Magnesium	Mg mg/l	1.13	1.08	1.02	1.25	-
Sodium	Na mg/l	9.0	7.0	8.4	9.1	-
Potassium	K mg/l	0.63	0.54	0.61	0.64	-
TRACE METALS						
Aluminium	Al mg/l	0.16	0.21	0.33	0.18	-
Iron	Fe mg/l	0.169	0.164	0.211	0.183	-
Manganese	Mn mg/l	0.009	0.014	0.012	0.011	-
NITROGEN						
Ammonia	N mg/l	-	-	-	-	-
Albuminoid	N mg/l	-	-	-	-	-
OTHER IONS						
Silica	Si mg/l	-	-	-	-	-
Total Phosphate	P mg/l	-	-	-	-	-
Fluoride	F mg/l	-	-	-	-	-
Total Dissolved Solids	mg/l	-	-	-	-	-

COMMENTS:

Raw water composition normal for this source of supply.

for Acting Director of Scientific Services

APPENDIX D

EXPERIMENTAL DATA - SECTION A

Dissolution test results : white water - day one

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)		
1	4.940	13.7	34.1	8.0	28.9	4.730	33.7	84.3	98.5	116.8	4.730	31.3	78.3	74.8	89.8
2	9.758	10.0	25.1	6.0	20.7	11.289	24.5	61.2	50.1	61.6	11.085	19.3	48.2	39.2	50.1
3	9.638	8.4	21.1	5.7	19.2	10.838	18.9	47.2	35.5	46.9	10.752	13.3	33.1	27.0	36.9
4	9.690	7.6	19.1	4.5	18.4	11.100	16.9	42.2	32.4	40.4	10.845	12.0	30.1	22.2	30.2
5	9.345	7.2	18.1	3.0	20.0	10.618	14.5	36.1	23.5	36.9	10.085	14.1	35.1	18.4	25.7
6	9.806	6.8	17.1	3.3	17.0	10.899	12.7	31.7	21.7	31.2	10.572	8.0	20.1	13.0	21.7
7	9.559	6.4	16.1	1.3	14.9	10.632	10.4	26.1	18.4	26.7	10.316	7.2	18.1	10.7	19.0
8	9.786	6.4	16.1	3.3	16.4	10.755	10.8	27.1	15.9	25.9	10.524	7.2	18.1	9.5	18.2
9	9.476	6.0	15.1	3.1	15.8	10.524	9.6	24.1	14.6	25.2	10.140	8.3	20.8	7.9	17.1
10	9.660	6.4	16.1	2.9	15.8	10.682	8.8	22.1	13.7	23.5	10.315	6.7	16.7	6.9	16.1
11	9.550	6.0	15.1	2.6	15.4	10.543	8.8	22.1	13.4	21.9	10.069	5.6	14.1	5.7	14.7
12	9.793	6.0	15.1	2.7	15.4	10.709	8.0	20.1	14.6	24.5	10.374	6.0	15.1	6.5	15.6
13	9.717	5.6	14.1	2.9	14.7	10.639	9.2	23.1	13.9	21.6	10.218	6.0	15.1	5.3	13.7
14	9.825	6.0	15.1	3.1	14.9	10.704	9.0	22.5	13.0	21.4	10.340	6.0	15.1	5.2	13.9
15	9.690	5.6	14.1	2.7	13.9	10.496	8.8	22.1	11.0	20.6	10.073	4.8	12.0	5.1	13.4
16	9.541	5.6	14.1	2.9	14.1	10.426	8.8	22.1	11.1	21.6	10.110	5.6	14.1	4.8	13.7
17	9.463	5.5	13.7		13.9	10.551	8.7	21.7		23.5	10.060	6.0	15.1		15.1
18	9.477	5.5	13.7		13.7	10.375	8.8	22.1		21.3	9.786	5.9	14.7		5.2
19	9.363	5.2	13.1		14.9	10.411	9.0	22.5		23.0	9.930	5.8	14.5		16.1
20	9.536	5.6	14.1		14.8	10.400	8.8	22.1		21.5	9.886	6.0	15.1		16.0
21	9.578	5.6	14.1		12.1	10.488	8.4	21.1		22.3	9.538	5.6	14.1		14.2
22	9.776	5.6	14.1		14.1	10.351	8.0	20.1		19.0	9.747	5.6	14.1		10.4
23	9.480	5.6	14.1		15.3	10.397	7.9	19.7		18.3	9.996	5.6	14.1		13.5
24	9.716	5.2	13.1		12.8	10.272	7.6	19.1		19.2	10.033	5.8	14.5		15.1
25		5.2	13.1				7.2	18.1							
26	9.619	5.6	14.1		14.4	10.245	7.2	18.1		19.6	9.936	5.9	14.7		13.3
27	9.508	5.5	13.9		13.5	10.408	7.6	19.1		20.1	9.629	5.8	14.5		13.3
28	9.844	5.5	13.7		13.3	10.272	7.9	19.7		21.2	9.907	5.6	14.1		15.4
29	9.621	5.6	14.1		13.4	10.444	7.6	19.1		19.6	9.747	5.5	13.7		13.3
30	9.365	5.2	13.1		13.2	10.203	7.2	18.1		19.9	9.968	5.2	13.1		12.5
31	9.428	5.2	13.1		13.2	10.296	7.2	18.1		17.3	9.698	5.5	13.7		14.3
32	9.422	5.2	13.1		13.1	10.068	6.8	17.1		17.6	9.672	5.2	13.1		13.6
33	9.360	5.2	13.1		12.8	10.105	7.2	18.1		17.5	9.801	5.5	13.7		12.3
34	9.505	5.2	13.1		13.0	10.294	7.6	19.1		20.3 *	9.734	5.2	13.1		11.9 *

Dissolution test results : white water - day two

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)		
1	4.94	16.9	42.2	8.0	28.9	4.73	48.2	120.5	98.5	116.8	4.73	41.0	102.4	74.8	89.8
2	9.65	12.4	31.1	7.0	25.5	11.50	34.5	86.3	74.8	91.1	11.41	26.5	66.3	60.4	73.1
3	9.56	10.4	26.1	6.3	19.5	11.27	28.1	70.3	59.1	73.8	11.09	21.7	54.2	43.6	55.4
4	9.89	9.2	23.1	4.5	25.0	11.37	25.7	64.3	32.4	66.8	10.85	18.5	46.2	22.2	48.4
5	9.77	8.8	22.1	3.0	20.0	11.10	22.5	56.2	23.5	56.7	10.84	14.5	36.1		35.0
6	9.81	8.8	22.1	3.3	23.4	10.90	16.9	42.2	21.7	41.7	10.57	12.9	32.1	13.0	31.7
7	9.41	7.2	18.1	3.2	18.7	10.87	16.1	40.2	30.7	42.2	10.65	11.2	28.1	18.7	29.5
8	9.75	7.6	19.1	4.3	18.5	10.95	16.1	40.2	27.4	40.1	10.74	11.2	28.1	17.7	27.9
9	9.59	7.9	19.7	3.8	19.5	10.90	15.4	38.6	28.5	38.7	10.52	13.1	32.6	14.9	26.1
10	9.65	7.2	18.1	3.4	18.9	11.04	13.7	34.1	26.1	36.7	10.63	8.8	22.1	12.7	23.7
11	9.65	8.0	20.1	5.1	19.7	10.86	14.1	35.1	26.7	36.7	10.28	8.8	22.1	13.0	24.0
12	9.51	7.2	18.1	3.4	18.3	10.72	12.9	32.1	25.7	36.2	10.34	8.8	22.1	12.0	22.6
13	9.73	7.4	18.5	3.6	18.2	10.89	13.7	34.1	22.3	34.1	10.47	8.8	22.1	10.6	21.3
14	9.85	7.2	18.1	3.6	18.2	10.86	14.5	36.1	20.6	33.1	10.49	8.0	20.1	9.9	20.6
15	9.70	7.6	19.1	3.3	17.5	10.84	14.5	36.1	21.6	32.2	10.32	8.0	20.1	8.7	19.5
16	9.81	7.1	17.7	3.4	17.7	10.93	12.9	32.1	22.3	32.6	10.42	8.0	20.1	8.7	19.9
17	9.68	7.1	17.7		19.6	10.73	13.0	32.6		33.2	10.30	8.0	20.1		
18	9.50	7.2	18.1		16.0	10.52	12.4	31.0		31.6	10.02	8.0	20.1		
19	9.91	7.2	18.1		19.3	10.72	12.4	31.0		30.6	10.06	7.6	19.1		
20	9.51	7.6	19.1		19.7	10.57	11.8	29.5		30.3	10.11	7.9	19.7		
21	9.84	7.5	18.7		18.1	10.39	11.8	29.5		29.4	9.96	7.9	19.7		
22	9.41	7.2	18.1		17.9	10.68	11.5	28.7		28.9	10.13	7.9	19.7		
23	10.06	6.4	16.1		16.8	10.82	11.5	28.7		30.7	10.42	7.6	19.1		
24	9.49	7.1	17.7		17.3	10.60	11.2	27.9		29.5	10.15	7.6	19.1		
25	9.93	7.1	17.7		17.9		10.6	26.4		28.4		7.2	18.1		
26	9.55	7.9	19.7		19.4	10.46	10.6	26.4		26.4	9.73	7.2	18.1		
27	9.78	6.8	17.1		17.2	10.53	10.1	25.1		22.1	9.98	7.2	18.1		
28	9.73	6.8	17.1		15.5	10.42	11.2	27.9		25.0	9.87	7.5	18.7		
29	10.26	7.0	17.5		17.5	10.93	10.6	26.4		26.8	10.36	7.2	18.1		
30	9.69	7.0	17.5		18.1	10.36	10.9	27.2		28.0	9.74	7.0	17.5		
31	9.84	6.9	17.3		18.1	10.79	10.6	26.4		26.3	10.45	6.4	16.1		
32	9.73	6.9	17.3		17.1	10.24	10.6	26.4		26.6	9.80	7.0	17.5		
33	9.54	6.4	16.1		17.2	10.24	9.9	24.8		26.8	9.92	6.8	17.1		
34	9.47	7.1	17.7		17.0	10.60	9.9	24.8		26.4 *	10.23	7.1	17.7		*

Dissolution test results : white water - day three

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)		
1		16.9	42.2	8.0	28.9	4.73	64.3	160.6	98.5	116.8		41.0	102.4	74.8	89.8
2	9.726	14.5	36.1	8.0	28.9	11.67	45.0	112.4	98.5	116.8	11.500	34.5	86.3	74.8	89.8
3	9.701	12.9	32.1	7.3	26.2	11.47	38.6	96.4	77.8	93.6	11.238	28.1	70.3	56.1	70.9
4	9.667	11.2	28.1	5.3	23.7	11.40	32.1	80.3	67.8	81.1	11.190	23.3	58.2	46.1	58.7
5	9.604	10.4	26.1	5.2	23.2	11.27	28.1	70.3	55.9	70.3	10.938	20.1	50.2	35.2	51.7
6	9.774	10.4	26.1	5.5	22.4	11.36	24.9	62.2	49.2	63.4	10.983	16.9	42.2	31.0	43.4
7	9.559	8.8	22.1	4.3	20.0	10.87	20.9	52.2	30.7	58.9	10.648	15.3	38.2	18.7	29.5
8	9.484	8.8	22.1	4.3	20.5	10.86	20.1	50.2	36.6	51.9	10.632	13.7	34.1	23.0	35.2
9	9.569	8.8	22.1	4.5	21.8	10.896	20.9	52.2	36.7	52.8	10.506	12.0	30.1	20.6	34.8
10	9.389	8.8	22.1	3.8	20.9	10.78	18.1	45.2	33.6	46.6	10.443	12.0	30.1	16.8	30.3
11	9.651	8.4	21.1	3.8	20.6	10.98	18.1	45.2	32.7	46.4	10.630	11.2	28.1	17.0	29.1
12	9.518	8.8	22.1	3.3	20.6	10.935	18.5	46.2	33.1	47.1	10.530	10.8	27.1	16.6	28.8
13	9.712	8.8	22.1	3.8	20.2	11.085	16.9	42.2	32.4	43.5	10.667	10.8	27.1	15.1	27.3
14	9.430	8.0	20.1	2.7	20.1	10.714	16.9	42.2	27.6	43.5	10.301	10.4	26.1	13.0	26.4
15	9.699	8.0	20.1	3.4	19.7	11.022	16.9	42.2	30.3	42.7	10.525	10.0	25.1	12.9	25.4
16	9.510	8.0	20.1	3.4	19.7	10.762	16.9	42.2	29.7	42.2	10.110	9.7	24.3	10.1	24.9
17	9.525	7.9	19.7	3.1	19.5	10.891	16.1	40.2	29.1	42.2	10.380	9.6	24.1	11.7	24.9
18	9.455	7.6	19.1	3.4	19.2	10.709	16.1	40.2	28.1	41.3	10.152	9.6	24.1	10.3	23.8
19	9.622	7.4	18.5	3.6	18.3	10.746	15.3	38.2	21.3	37.7	10.379	8.8	22.1	10.6	23.1
20	9.505	8.0	20.1	3.3	18.2	10.735	15.3	38.2	26.1	38.1	10.201	8.8	22.1	9.9	21.4
21	9.578	7.2	18.1	3.1	19.2	10.826	14.9	37.1	24.0	37.4	10.345	8.8	22.1	9.8	22.1
22	9.474	8.0	20.1	3.1	18.9	10.684	14.9	37.1	25.0	37.4	10.126	8.8	22.1	9.1	21.8
23	9.573	7.2	18.1	3.3	18.7	10.732	14.5	36.1	23.1	36.3	10.318	9.1	22.7	9.9	21.4
24	9.443	7.2	18.1	2.9	18.5	10.603	13.7	34.1	23.7	35.7	10.136	8.0	20.1	9.1	21.1
25		7.2	18.1				13.7	34.1				8.8	22.1		
26	9.349	8.0	20.1	2.7	17.8	10.575	13.0	32.5	20.6	32.2	10.059	8.0	20.1	7.0	18.5
27	9.503	7.6	19.1	2.9	17.5	10.743	14.5	36.1	20.6	33.6	10.165	8.0	20.1	7.9	19.9
28	9.448	7.2	18.1	2.7	18.3	10.603	13.7	34.1	22.1	33.9	10.056	7.2	18.1	7.5	19.9
29	9.630	6.8	17.1	3.1	18.0	10.78	14.1	35.1	23.3	36.0	10.175	8.0	20.1	9.6	20.2
30	9.334	7.6	19.1	2.1	18.9	10.532	13.7	34.1	20.2	34.3	9.930	8.0	20.1	6.9	19.2
31	9.490	8.0	20.1	2.1	18.0	10.628	13.7	34.1	20.1	31.9	10.133	7.6	19.1	6.3	18.7
32	9.391	7.6	19.1	2.2	17.1	10.392	12.9	32.1	17.1	30.9	9.980	7.6	19.1	6.7	19.2
33	9.421	7.6	19.1	2.4	17.7	10.43	12.9	32.1	15.9	31.2	10.113	8.4	21.1	6.7	18.7
34	9.482	7.6	19.1	2.4	17.7 *	10.626	13.7	34.1	21.9	33.8 *	10.044	7.6	19.1	6.9	19.2 *

Dissolution test results : brown water - day one

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)		
1	9.000	18.5	42.2	1.7	23.0		29.2	68.9	67.1	89.8		25.7	60.3	44.4	66.4
2	8.866	15.4	34.6	3.8	31.2	10.895	26.7	62.7	28.7	43.9	10.568	19.7	45.2	16.7	32.0
3	8.587	14.1	31.1	1.0	20.4	10.422	19.3	44.2	10.3	23.4	10.092	14.5	32.1	10.3	23.4
4	8.609	13.3	29.1	0.8	17.9	10.636	16.5	37.2	16.0	28.9	9.993	13.7	30.1	6.7	19.9
5	8.118	12.4	27.1	0.4	20.9	10.180	16.1	36.2	11.0	26.4	9.615	12.4	27.1	3.3	17.0
6	8.029	11.6	25.1	-0.5	14.7	10.198	14.5	32.1	8.7	20.5	9.564	11.2	24.1	3.0	16.0
7	7.715	10.8	23.1	-1.0	13.1	9.464	14.1	31.1	5.7	18.7	9.123	11.2	24.1	1.2	13.9
8	7.721	9.6	20.1	-0.6	12.9	10.069	13.7	30.1	6.5	19.2	9.005	9.6	20.1	0.5	12.5
9	7.665	11.6	25.0	-1.1	16.0	9.596	14.1	31.1	4.3	20.4	8.464	10.4	22.1	0.2	15.1
10	7.660	11.2	24.1	-1.5	16.6	9.563	12.9	28.1	3.3	19.7	8.287	10.4	22.1	0.6	15.5
11	7.440	10.4	22.1	-2.2	14.0	9.278	12.0	26.1	2.4	18.0	8.138	10.4	22.1	-0.1	15.5
12	7.540	9.6	20.1	-2.3	13.1	9.574	11.2	24.1	2.4	18.0	8.259	9.6	20.1	-0.1	13.8
13	7.350	8.8	18.1	-2.7	11.4	9.200	10.4	22.1	1.4	15.8	7.882	8.8	18.1	-1.0	13.2
14	7.392	8.8	19.1	-2.2	12.1	9.470	10.8	23.1	2.2	17.1	8.011	9.2	19.1	-0.3	11.9
15	7.168	8.0	16.1	-2.9	9.4	9.377	10.4	22.1	1.9	16.8	7.732	8.8	18.1	-0.8	8.0
16	7.165	8.0	16.1	-2.9	9.4	9.300	10.4	22.1	1.7	16.5	7.810	8.8	18.1	-1.3	9.2
17	7.974	7.5	14.7		8.4	10.361	9.6	20.1		14.0	9.374	14.5	32.3		8.2
18	7.976	7.9	15.7		5.3	10.232	9.2	19.1		12.8	9.270	14.7	32.7		5.4
19	8.111	7.6	15.1		5.0	10.335	9.0	18.6		11.1	9.360	14.0	31.1		7.5
20	7.926	8.4	17.1		9.9	10.187	8.8	18.1		12.8	9.137	14.0	31.1		9.1
21	7.833	7.2	14.1		5.1	10.337	9.3	19.3		12.0	9.215	13.8	30.5		10.9
22	7.887	7.9	15.7		5.1	10.093	9.2	18.9		8.4	9.009	13.6	30.1		9.5
23	7.912	7.9	15.8		7.7	10.239	9.1	18.8		11.4	9.200	13.6	30.1		9.4
24	7.728	8.5	17.3		10.3	10.102	8.8	18.1		11.8	8.750	13.3	29.3		8.4
25		7.2	14.1		4.4		9.5	19.8		10.1		12.0	26.1		
26	7.695	7.3	14.3		6.1	10.002	8.6	17.6		6.8	8.805	11.6	25.1		5.5
27	7.735	6.9	13.3		5.3	10.024	8.8	18.0		7.4	8.413	12.4	27.1		6.8
28	7.616	6.9	13.4		4.9	10.026	8.8	18.0		3.9	8.583	12.0	26.1		6.8
29	7.922	7.2	13.9		3.8	10.238	9.3	19.2		10.0	8.996	12.2	26.5		3.3
30	7.709	7.1	13.7		-0.7	10.050	9.2	19.0		6.3	8.477	12.0	26.1		1.0
31	7.949	7.2	14.0		-1.0	10.095	9.4	19.5		5.1	8.749	12.0	26.1		4.2
32	7.726	7.0	13.5		3.9	10.028	9.5	19.7		7.8	8.489	12.0	26.1		5.0
33	7.745	6.9	13.1		2.1	10.122	9.2	18.9		7.4	8.233	12.0	26.1		5.1
34	7.881	6.8	13.0		7.5 *	9.993	9.1	18.8		6.1	8.707	12.8	28.1		5.5 *

Dissolution test results : brown water - day two

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3		)		(mgCa/l)	(all mg/L as CaCO3		)		(mgCa/l)	(all mg/L as CaCO3		)
1	9.000	23.7	55.2	1.7	23.0		44.2	106.4	67.1	89.8		36.5	91.4	44.4	66.4
2	9.173	19.3	44.2	2.8	26.0	10.895	34.5	82.3	28.7	43.9	10.568	25.7	64.3	16.7	32.0
3	9.082	16.9	38.2	3.0	25.4	10.422	28.1	66.3	10.3	23.4	10.092	22.5	56.2	10.3	23.4
4	8.609	16.1	36.2	0.8	21.7	10.636	25.7	60.3	16.0	28.9	9.993	20.5	51.2	6.7	19.9
5	8.118	14.1	31.1	0.4	18.4	10.180	23.3	54.2	11.0	26.4	9.615	16.9	42.2	3.3	17.0
6	8.029	14.1	31.1	-0.5	16.7	10.198	21.3	49.2	8.7	20.5	9.564	15.4	38.6	3.0	16.0
7	8.260	13.7	30.1	.0	19.6	9.464	20.1	46.2	5.7	18.7	9.123	14.1	35.1	1.2	13.9
8	8.475	12.9	28.1	0.2	19.2	10.069	18.5	42.2	6.5	19.2	9.005	13.7	34.1	0.5	12.5
9	8.179	14.3	31.7	-0.8	20.4	9.596	17.7	40.2	4.3	20.4	8.464	12.9	32.1	0.2	15.1
10	8.109	12.9	29.1	0.2	21.4	9.563	17.3	39.2	3.3	19.7	8.287	13.3	33.1	0.6	15.5
11	8.060	12.0	26.1	0.6	16.6	9.278	16.9	38.2	2.4	18.0	8.138	12.4	31.1	-0.1	15.5
12	8.033	12.0	26.1	-0.6	18.8	9.574	16.1	36.2	2.4	18.0	8.259	12.4	31.1	-0.1	13.8
13	7.965	11.2	24.1	-0.6	16.6	9.200	15.3	34.2	1.4	15.8	7.882	13.7	34.1	-1.0	13.2
14	8.030	10.8	23.1	-0.8	17.1	9.470	15.3	34.2	2.2	17.1	8.011	10.8	27.1	-0.3	11.9
15	7.861	10.4	22.1	-1.0	15.0	9.377	14.5	32.1	1.9	16.8	7.732	11.2	28.1	-0.8	8.0
16	7.951	10.8	23.1	-0.8	15.9	9.300	14.7	32.7	1.7	16.5	7.810	12.0	30.1	-1.3	9.2
17	7.974	10.3	21.7		12.8	10.361	15.9	35.8			9.374	10.5	22.3	-1.3	9.2
18	7.976	9.9	20.7		9.4	10.232	13.3	29.2			9.270	10.7	22.7	-1.3	9.2
19	8.111	10.4	22.1		15.3	10.335	14.9	33.1			9.360	10.8	23.1	-1.3	9.2
20	7.926	9.2	19.1		9.5	10.187	14.1	31.1			9.137	9.6	20.1	-1.3	9.2
21	7.833	10.4	22.1		14.8	10.337	14.5	32.1			9.215	11.0	23.5	-1.3	9.2
22	7.887	10.0	21.1		13.5	10.093	14.1	31.1			9.009	10.4	22.1	-1.3	9.2
23	7.912	9.7	20.3		14.3	10.239	14.1	31.3			9.200	10.3	21.7	-1.3	9.2
24	7.728	10.8	23.1		16.0	10.102	14.9	33.1			8.750	10.8	23.1	-1.3	9.2
25		8.0	16.1		8.8		13.6	30.0				8.8	18.1	-1.3	9.2
26	7.695	9.2	19.1		10.2	10.002	12.6	27.6			8.805	8.0	16.1	-1.3	9.2
27	7.735	8.8	18.1		6.8	10.024	13.3	29.1			8.413	8.4	17.1	-1.3	9.2
28	7.616	8.0	16.1		9.3	10.026	12.9	28.1			8.583	8.0	16.1	-1.3	9.2
29	7.922	8.3	16.7		7.1	10.238	12.3	26.7			8.996	8.4	17.1	-1.3	9.2
30	7.709	8.0	16.1		8.8	10.050	12.0	26.1			8.477	8.0	16.1	-1.3	9.2
31	7.949	8.3	16.7		9.1	10.095	12.7	27.7			8.749	8.3	16.7	-1.3	9.2
32	7.726	8.0	16.1		10.0	10.028	12.0	26.1			8.489	8.0	16.1	-1.3	9.2
33	7.745	8.0	16.1		9.0	10.122	11.9	25.7			8.233	8.0	16.1	-1.3	9.2
34	7.881	9.1	18.7		11.5 *	9.993	12.7	27.7		*	8.707	9.1	18.7	-1.3	9.2 *

Dissolution test results : brown water - day three

	CARBONATED OPC					UNCARBONATED OPC					UNCARBONATED 30% fly ash				
CYCLE	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK	PH	CALCIUM	CALCIUM	HCO3 ALK	H2CO3 ALK
		(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)				(mgCa/l)	(all mg/L as CaCO3)		
1		24.1	60.2	3.8	31.2		44.2	110.4	67.1	89.8		36.5	91.4	44.4	66.4
2	9.218	21.7	54.2	3.8	31.2	11.45	43.4	108.4	67.1	89.8	11.18	32.1	80.3	44.4	66.4
3	9.149	19.3	48.2	3.8	27.7	11.18	35.3	88.4	53.4	73.6	11.18	27.3	68.3	32.5	53.1
4	9.072	17.7	44.2	2.0	25.9	11.11	32.9	82.3	43.4	64.1	10.74	23.3	58.2	24.2	44.4
5	8.972	16.9	42.2	3.1	26.3	10.93	28.9	72.3	36.3	56.7	10.55	21.3	53.2	19.9	38.4
6	9.028	15.3	38.2	1.5	23.0	11.01	26.5	66.3	32.7	49.7	10.58	19.7	49.2	16.4	34.2
7	8.644	15.3	38.2	1.0	22.2	10.70	24.1	60.2	24.5	43.4	10.18	17.3	43.2	10.7	28.5
8	8.330	14.6	36.5	-0.5	21.3	10.536	22.5	56.2	22.5	41.7	9.924	16.9	42.2	8.5	26.9
9	8.648	15.2	37.9	0.9	24.3	10.514	22.5	56.2	21.6	44.6	9.845	16.1	40.2	8.2	29.1
10	8.284	14.5	36.1	1.3	24.8	10.331	20.9	52.2	18.5	38.4	9.569	15.3	38.2	4.8	25.4
11	8.503	14.1	35.1	0.7	22.7	10.392	20.1	50.2	16.1	38.7	9.767	15.7	39.2	5.0	25.5
12	8.345	14.5	36.1	0.0	21.9	10.419	19.4	48.6	17.7	38.6	9.551	14.5	36.1	3.8	24.3
13	8.424	13.7	34.1	0.0	21.6	10.513	19.3	48.2	15.6	35.3	9.594	13.3	33.1	3.3	22.6
14	8.046	13.0	32.5	-0.3	20.2	10.228	19.3	48.2	14.9	35.0	9.411	12.9	32.1	3.1	21.8
15	8.03	12.9	32.1	-0.8	18.4	10.458	18.5	46.2	15.4	35.1	9.485	12.9	32.1	3.1	20.4
16	7.951	13.0	32.5	-0.8	18.6	10.242	19.3	48.2	14.9	34.3	9.265	13.0	32.5	2.4	20.7
17	7.974	12.7	31.7	-0.8	18.3	10.361	18.5	46.2	14.7	33.8	9.374	12.9	32.3	2.4	20.2
18	7.976	12.3	30.7	-0.8	18.1	10.232	17.7	44.2	14.4	32.6	9.27	13.1	32.7	2.4	19.5
19	8.111	12.0	30.1	-0.8	16.6	10.335	16.5	41.2	12.0	29.3	9.36	12.4	31.1	2.4	17.7
20	7.926	12.0	30.1	-0.8	16.6	10.187	16.9	42.2	11.8	28.5	9.137	12.4	31.1	1.7	17.8
21	7.833	11.6	29.1	-0.6	15.9	10.337	16.9	42.2	12.0	29.3	9.215	12.2	30.5	1.5	17.1
22	7.887	11.6	29.1	-0.8	16.6	10.093	17.0	42.6	11.3	29.0	9.009	12.0	30.1	1.7	17.8
23	7.912	11.5	28.7	-0.8	15.9	10.239	17.0	42.6	12.3	30.5	9.2	12.0	30.1	1.5	17.1
24	7.728	11.7	29.3	-1.3	16.2	10.102	16.9	42.2	10.3	27.1	8.75	11.7	29.3	0.5	16.1
25		9.6	24.1				16.9	42.2				10.4	26.1		
26	7.695	11.2	28.1	-0.8	15.4	10.002	15.3	38.2	8.9	24.9	8.805	10.0	25.1	0.7	15.3
27	7.735	11.2	28.1	-0.6	16.0	10.024	15.3	38.2	8.2	26.1	8.413	10.8	27.1	0.0	15.9
28	7.616	10.4	26.1	-0.8	15.9	10.026	14.5	36.1	8.9	26.7	8.583	10.4	26.1	0.3	15.9
29	7.922	10.4	26.1	-0.8	15.9	10.238	16.1	40.2	11.0	27.1	8.996	10.6	26.5	1.2	15.6
30	7.709	10.4	26.1	-1.3	14.2	10.050	14.9	37.1	9.3	25.0	8.477	10.4	26.1	0.7	15.4
31	7.949	10.4	26.1	-1.0	15.2	10.095	14.9	37.1	10.3	25.0	8.749	10.4	26.1	0.5	14.4
32	7.726	10.4	26.1	-0.8	14.8	10.028	15.3	38.2	8.2	23.7	8.489	10.4	26.1	0.2	13.7
33	7.745	10.4	26.1	-1.1	14.7	10.122	14.9	37.1	8.6	24.5	8.233	10.4	26.1	0.0	14.1
34	7.881	11.2	28.1	-0.8	15.4	9.993	15.3	38.2	8.6	24.5	8.707	11.2	28.1	0.5	14.4

APPENDIX E

EXPERIMENTAL DATA - SECTION B

Series One Test Results : carbonation depth with time measurements

Time (days)	sample 1 (mm)	sample 2 (mm)	sample 3 (mm)	sample 4 (mm)	sample 5 (mm)	sample 6 (mm)
0	5.4	3.7	4.1	3.1	2.0	1.4
1	8.0	5.9	5.0	3.8	5.2	2.8
3	10.4	7.3	7.9	6.8	6.6	5.0
5	13.8	10.3	8.9	8.9	8.7	6.0
7	14.6	12.0	10.8	9.9	9.7	7.1
11	21.8	15.0	13.1	11.7	10.0	8.8
17	25.0	17.0	15.6	13.8	9.5	10.0
25	----	25.0	19.5	15.4	14.6	12.5
35	----	----	25.0	25.0	----	----
38	----	----	----	----	17.9	25.0

Series Two Test Results : carbonation depth with time measurements

Time (days)	sample 7 (mm)	sample 8 (mm)	sample 9 (mm)	sample 10 (mm)	sample 11 (mm)	sample 12 (mm)
0	0.0	0.0	0.0	1.1	0.9	2.0
1	1.3	1.8	2.4	3.1	3.1	5.2
3	3.5	3.4	4.3	4.7	5.3	6.6
5	4.9	3.9	5.3	5.7	5.7	8.7
7	5.4	5.0	6.2	7.6	7.9	9.7
11	6.9	6.2	6.9	8.8	9.4	10.0
17	7.7	7.5	10.8	10.5	10.5	9.5
25	10.8	12.0	12.5	12.6	12.6	14.6
35	13.8	14.3	16.1	15.9	19.0	17.9
45	15.6	16.0	16.8	17.3	----	----
47	----	18.9	----	----	----	----
58	22.4	----	----	----	----	----