Softening and Stabilization of Municipal Waters

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SOFTENING AND STABILIZATION OF MUNICIPAL WATERS

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Foreword

Unstable water can be corrosive, aggressive and scale-forming. These characteristics in turn can result in the following undesirable consequences: deterioration in water quality (e.g. dissolution of metals such as lead, cadmium, copper, zinc and iron); turbidity; tastes and odours; loss in conduit-carrying capacity; drop in pressure; water loss from perforations in conduits; pump replacement; increased maintenance costs; and in extreme cases — conduit and structural failure with associated high replacement cost.

Problems experienced with water softening and stabilization in the water industry were highlighted in the late seventies during research and development studies on water reclamation. Difficulties experienced at the Windhoek Water Reclamation Plant (South West Africa/Namibia) and at the experimental Stander Water Reclamation Plant (Pretoria), led the Water Research Commission to initiate research in this field. The Water Resources and Public Health Engineering Division of the Department of Civil Engineering at the University of Cape Town, South Africa — an internationally acknowledged specialist centre in this field — was contracted to research selected problems in this field.

This monograph is aimed at the chemist and designer in the water industry. It gives guidelines for the softening and stabilization of municipal waters as well as detailed background information. Some worked examples, to demonstrate the practical application of the guidelines, are included.

The reader should note that guidelines rather than absolute criteria are presented. This was done in recognition of the fact that knowledge in this field is still limited and will require further research and development. Where specific solutions are required, it is recommended that the authors or other knowledgeable experts be consulted.

P. E. Odendaal
Executive Director
Water Research Commission

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DEFINITIONS AND SYMBOLS

ACIDITY

acidity = general term for the proton (H^+) donating capacity relative to some equivalent solution

CO_3^{2-} acidity = proton donating capacity relative to an equivalent solution of CO_3^{2-}. Also called total acidity or Acidity
Note: a letter underlined, i.e. A, denotes that A in the text is in capital letters, e.g. Acidity, Alkalinity

HCO_3^- acidity = proton donating capacity relative to an equivalent solution of HCO_3^-. Also called CO_2 acidity

$H_2CO_3^*$ acidity = proton donating capacity relative to an equivalent solution of $H_2CO_3^*$. Also called mineral acidity

CO_3^{2-} acidity = total acidity or Acidity (old nomenclature)

HCO_3^- acidity = CO_2 acidity (old nomenclature)

$H_2CO_3^*$ acidity = mineral acidity (old nomenclature)

ACTIVITY

activity = active molar concentration, moles/ℓ
(i) = activity of species 'i', i.e. active concentration of species i, moles/ℓ

ACTIVITY COEFFICIENT

f_i = activity coefficient of species 'i' on the molar scale

ALKALINITY

alkalinity = general term for the proton (H^+) accepting capacity relative to some equivalent solution

CO_3^{2-} = proton accepting capacity relative to an equivalent solution of CO_3^{2-}. Also called caustic alkalinity

HCO_3^- = proton accepting capacity relative to an equivalent solution of HCO_3^-. Also called phenolphthalein alkalinity

$H_2CO_3^*$ alkalinity = proton accepting capacity relative to an equivalent solution of $H_2CO_3^*$. Also called total alkalinity or Alkalinity

CO_3^{2-} alkalinity = caustic alkalinity (old nomenclature)

HCO_3^- alkalinity = phenolphthalein alkalinity (old nomenclature)

$H_2CO_3^*$ alkalinity = total alkalinity or Alkalinity (old nomenclature)

BUFFER CAPACITY

β = buffer capacity, moles $H^+/\ell/pH$.

CONCENTRATION

[ ] = molar concentration, also called concentration, moles/ℓ.

[i] = molar concentration of species 'i', moles i/ℓ.

( ) = active molar concentration, also called activity, moles/ℓ.

(i) = activity of species 'i', moles/ℓ.

{ } = equivalent concentration, equivalents/ℓ.

{i} = equivalent concentration of species 'i'.

'no brackets' = concentration in mg/ℓ expressed as $CaCO_3$ ($CaCO_3$ equivalent scale).

C_T = total concentration of dissolved inorganic carbonate species expressed on the same scale as the component carbonate species, i.e. moles/ℓ, or equivalents/ℓ or mg/ℓ expressed as $CaCO_3$.

EQUILIBRIUM CONSTANTS

K_i = equilibrium constant for a particular reaction with all species expressed as activities, e.g. $(H^+)(HCO_3^-)/(H_2CO_3^*) = K_1$

K'_{a1} = apparent equilibrium constant for a particular reaction with all species expressed as concentrations (mol/ℓ), e.g. $[H^+][HCO_3^-]/(H_2CO_3^*) = K'_{a1}$

K'_1 = apparent equilibrium constant for a particular reaction with H^+ expressed as activity and all other species expressed as concentrations, e.g. $(H^+)[HCO_3^-]/[H_2CO_3^*] = K'_1$

EQUIVALENT SOLUTIONS AND EQUIVALENCE POINTS

Equivalent solution = addition of a salt or acid of a weak acid base system to pure water.
(Note: equivalent solution is not related to mass equivalents as used within concentration units).

Equivalence point = pH established for an equivalent solution is called the equivalence point. For example, addition of Na_2CO_3 to pure water gives a CO_3^{2-} equivalent solution with a corresponding pH (equivalence point). The equivalence point depends on the mass of CO_3^{2-} added.

pX NOTATION

pH = negative logarithm of the hydrogen ion activity
= $-\log_{10}(H^+)$.

pe = negative logarithm of the electron activity.

PARTIAL PRESSURE

$\bar{p}O_2$ = partial pressure of oxygen in atmospheres

$\bar{p}CO_2$ = partial pressure of carbon dioxide in atmospheres.

Disclaimer

The views expressed in this Monograph are those of the authors and do not necessarily constitute endorsement or recommendation by the Water Research Commission or the University of Cape Town.

Chapter 1

Introduction

Water sources for municipal supplies range over a wide spectrum of chemical quality. At the one end are waters having virtually no dissolved solids, with low Alkalinity and pH; typical examples are waters derived from the Table Mountain sandstone regions in South Africa. At the other end are waters having high concentrations of dissolved solids (including calcium, magnesium, sodium, chloride and sulphate ions) with high Alkalinity and variable pH and, where no oxygen is present, high concentrations of dissolved iron, manganese and possibly carbon dioxide; underground waters probably constitute the main ones in this category. Between these extremes waters with virtually any combination of chemical quality may be found, reflecting the history of the water and the region from which it is derived.

Most waters will require some form of treatment before discharge to a distribution system. The chemical quality of the water entering the system always has some impact on the system, ranging from negligible to severe. Waters with the appropriate qualities have minimal impact, and the systems have long life expectation; waters with inappropriate qualities can have a major impact and reduce expectation of the lives of systems substantively. Impact of such waters on the system sorts into the following three kinds:

(i) The water may cause extensive precipitation of calcium and iron minerals on the walls of the conduits, so extensive that the carrying capacity of the conduit may be reduced severely, to zero on occasion.

(ii) The water may dissolve away the cement matrix in asbestos cement and concrete conduits and water retaining structures, causing destruction of the integrity of the material. This effect is designated by the term aggression.

(iii) Electro chemical reactions between the water and metal components of the system may give rise to dissolution of the metal and precipitation of metal salts resulting in pitting, nodule formation, red water, etc., destruction of the conduit and loss of function are the end results. These effects are designated by the term corrosion.

Economic costs in maintaining distribution systems have not been estimated country-wide in South Africa, but must be substantial. A study in this regard is long overdue but qualitative discussions with municipal officials in charge of water supplies, and with consumers, have forced the conclusion that problems with corrosion and aggression in water distribution systems indeed are widespread. In many instances, but not in all, these effects can be nullified or minimized by relatively simple corrective chemical pretreatment. Appropriate treatment, however, demands an understanding of the underlying chemistry of the water and the interactions between the water and the material of the retaining structure.

Extensive research has been conducted into the chemistry of water in the treatment of water supplies. Perhaps the most influential research contribution has been that of Langelier in 1936. He recognized the importance of (1) the carbonate system in establishing pH in water, and (2) the solubility of the calcium carbonate mineral in establishing a state of under- or oversaturation. Under- and oversaturated states he linked to aggressive/ corrosive and non-aggressive/non-corrosive states respectively. He proposed that the water be treated to a state of oversaturation (supersaturation) which would cause a layer of calcium carbonate to precipitate out on walls containing the water thereby providing an isolating protective film. To assess the saturation state he developed an index, the Langelier Saturation Index, based on equilibrium chemistry in terms of the calcium and alkalinity concentrations and pH. He proposed criteria in terms of the index to prevent aggression and corrosion. Chemical treatment to adjust water to a desired state of non-aggressiveness/non-corrosiveness has been described generally by the term stabilization.

Although fifty years have passed since the pioneering work of Langelier, his criteria for protection of distribution systems are still applied, one can almost say, indiscriminately. Since Langelier's work extensive research studies have been conducted into the chemistry of the carbonate system itself, and the chemical response of water in contact with iron metals and cement materials. Influence of other factors, such as chloride and sulphate ions, total concentration of dissolved salts, pH, dissolved oxygen concentration, velocity of flow etc., have been more clearly delineated, though by no means resolved. This is true, in particular, with regard to corrosion.

Unfortunately information on conditioning of the water to minimise aggression and corrosion has not been applied as widely as its importance merits. One reason for this is that the information is 'buried' in many journals, often ones not readily available or not recognized by chemists controlling water treatment works as sources of information. Such a situation is clearly an undesirable one when one considers the large amounts of capital invested in water treatment and distribution systems.

In South Africa an extremely wide range of chemical water qualities serve as sources for municipal supplies, a situation often not applying to countries of more limited geographical, hydrological or geological extent. Water chemists and water engineers in this country, therefore, must be cognisant of the problems associated with water/system material interactions in the broadest context if mistakes in design and operation are to be minimized.

In this monograph the authors have endeavoured to collect and rationalize all the information on water stabilization they have had access to. Brief descriptions of the chemistry of aggression and corrosion are given to serve as a background to the development of criteria for ameliorating adverse effects. Because corrosion and passivation are extremely complex and still only partially understood, the guide lines are based in part on incomplete information and should not be taken as absolute criteria; on occasion factors, perhaps not as yet identified as significant, may be present that invalidate the guide lines, for example, effects of dissolved organic material, silicates and phosphates on both aggression and corrosion.

Quantitative procedures are described to estimate dosages of chemicals to be applied to a water to attain the desired quality. These procedures are all based on chemical equilibrium theory. The theory is quite complex and in its analytical form one can hardly expect chemists to use it in day to day operation of a water works. However, in recent years graphical presentation of the calcium-carbonate system, in terms of parameters in normal usage (e.g. Alkalinity, Acidity, pH and calcium concentration), has allowed rapid practical solutions to be obtained satisfying chemical equilibrium theory. However, it should be noted that in certain situations equilibrium is attained only slowly; attention is drawn to these situations in the text.

Although dosage calculations now can be made with ease, this does not mean necessarily that the problem of corrosion (in particular) is resolved. Understanding of corrosion phenomena and its amelioration in mild steel and cast iron pipes is still very incomplete, particularly where waters contain chloride and sulphate ions. Waters with appreciable concentrations of these ions, unfortunately, are not uncommon in South Africa so that substantive criteria cannot yet be formulated whereby corrosion can be optimally reduced, or, when it becomes provident to dispense with ferrous conduits and replace these by asbestos cement, concrete or plastic.

Chapter 2

Aggression of Water to Cement and Concrete Materials

2.1 INTRODUCTION

Aggression is the designation given to the phenomena where water contained in cement and concrete lined structures attacks the cement matrix. Two distinct aggressive processes have been identified: (1) The water has chemical characteristics that cause dissolution of some of the minerals in the cement matrix. (2) The water contains sulphate species which might react chemically with some of the minerals in the cement matrix to form products which cause physical disruption of the matrix.

The forms of aggression above arise as follows: Hardened cement in concrete and sand-cement consists of a matrix mainly of free lime, magnesium oxide, hydrated di- and tricalcium silicates, tricalcium aluminates and tetracalcium alumino ferrites, Fulton (1977). With regard to chemical dissolution, at the outer surfaces of the cement mass the free lime, $Ca(OH)_2$, will react with carbon dioxide either in the air or dissolved in the water, to form a calcium carbonate precipitate. If the chemical characteristic of the water is such that it causes dissolution of calcium carbonate, mineral will be removed from the matrix, starting from the outer surface and in cracks, penetrating progressively deeper into the concrete mass, in this fashion weakening the matrix strength. This form of aggression can be prevented by changing the chemical characteristics of the water such that it will not dissolve calcium carbonate in the cement matrix.

With regard to sulphate attack, when the dissolved sulphate concentration is high the hydrated calcium oxide, aluminates and alumino ferrite react with the sulphate species to form sulphate minerals that occupy greater volumes than the original minerals causing swelling and consequent physical disintegration of the cement matrix. Furthermore, hydrated calcium silicate also reacts with sulphate ions forming a product which has a much lower strength than the original mineral. As hydrated calcium silicate is the mineral that contributes the most to the strength of the matrix, chemical changes of the silicates due to reaction with the sulphates significantly reduce the structural strength of the matrix. The volumetric changes, together with the weakening of the hydrated silicates, can have a very adverse effect on the integrity and strength of the cement material, Lea (1949). To suppress these effects (i.e. to terminate this form of aggression) special types of cement and a high density concrete need to be used.

2.2 CALCIUM CARBONATE DISSOLUTION AND PRECIPITATION

2.2.1 The saturation state

The terms undersaturation, supersaturation and saturation with respect to calcium carbonate describe chemical states in a water such that it respectively, dissolves solid calcium carbonate (undersaturation), precipitates solid calcium carbonate out of solution (supersaturation) and neither precipitates nor dissolves calcium carbonate (saturation). Theoretically these states are identified by comparing the activity product of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species with the solubility product constant for calcium carbonate, K_{sp}.

The activity product is given by the product of the active molar concentrations of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species, i.e.

Activity product = $(Ca^{2+}).(CO_3^{2-})$

where () = active molar concentration.

The activity product cannot increase ad lib but has a stable upper limit called the solubility product. If the activity product is less than the solubility product, solid calcium carbonate dissolves into the water until the activity product equals the solubility product, if greater, solid calcium carbonate will precipitate out of the water again until the two products are equal; if equal, there will be no net dissolution or precipitation. Accordingly, for dissolution of calcium carbonate (undersaturation),

$$(Ca^{2+})(CO_3^{2-}) < K_{sp} \qquad (2.1a)$$

for precipitation of calcium carbonate (supersaturation),

$$(Ca^{2+})(CO_3^{2-}) > K_{sp} \qquad (2.1b)$$

and, at saturation,

$$(Ca^{2+})(CO_3^{2-}) = K_{sp} \qquad (2.1c)$$

where K_{sp} = solubility product of the mineral precipitated
( ) = "active" concentration (activity) of the ion.

In Eqs (2.1a, 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 concentrations and types of salts present in solution), state of supersaturation, temperature and pressure. Determination of thermodynamic solubility products is beset with many difficulties which will not be considered here; for the purpose of this publication their existence and their magnitudes as recorded in the literature, are accepted as base reference constants in the description of precipitation behaviour. For low ionic strength waters in the temperature range 0-60°C, at low degrees of supersaturation and atmospheric pressure, the usual calcium carbonate mineral that will precipitate, is calcite. Accordingly, in distribution systems carrying water for general municipal use, should calcium carbonate precipitate, calcite will be the expected mineral. Even in water softening units operating under steady state conditions, the degree of supersaturation still is sufficiently low that calcite is the expected precipitant. Calcite therefore constitutes the normal precipitant in stabilization and softening processes. The calcite solubility product is temperature dependent as follows, Loewenthal and Marais (1976),

$$pK_{sp} = 8{,}03 + 0{,}01183.T \qquad (2.2)$$

where $pK_{sp} = -\log_{10} K_{sp}$

$= 8{,}32$ at 25°C

T = degrees Celsius.

In Eq 2.1 the "active concentrations" of the ions, (Ca^{2+}) and (CO_3^{2-}), are the <u>effective</u> or <u>reactive</u> concentrations not the true or stoichiometric concentrations. The effective concentrations are called "activities", and the stoichiometric concentrations are called "concentrations".* Conventionally, activity is signified by round brackets, (), and concentration by square brackets, [].

The concentration is linked to the activity via an activity coefficient. For example

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

where (Ca^{2+}) = Ca^{2+} activity (moles/ℓ)
$[Ca^{2+}]$ = Ca^{2+} stoichiometric concentration (moles/ℓ)
f_D = activity coefficient for an ion with two charges, i.e. a divalent ion. (For municipal water supplies the value of the activity coefficient is always less than unity.)

i.e.

$$(Ca^{2+})(CO_3^{2-}) = f_D\,[Ca^{2+}].f_D\,[CO_3^{2-}] \qquad (2.3)$$

The right hand side of Eq (2.3) is more useful in practical work because the stoichiometric concentrations are the ones which are measured by chemical means or estimated directly or indirectly from associated chemical measurements. Consequently, <u>for say saturation,</u>

$$[Ca^{2+}][CO_3^{2-}] = K_{sp}/f_D^2 = K'_{sp} \qquad (2.4)$$

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

The estimation of the saturation state†, utilizing Eq (2.4), requires quantitative values for $[CO_3^{2-}]$, $[Ca^{2+}]$, f_D and K_{sp}: The concentrations $[CO_3^{2-}]$ and $[Ca^{2+}]$ are

---

* The convention of calling "stoichiometric concentration" by the abbreviation "concentration" may fall strangely on the ears of non-chemists but must be accepted as standard chemical nomenclature. This convention will be adhered to throughout the monograph.

† Description of the saturation state can be given in terms of the Langelier Saturation Index and/or the $CaCO_3$ precipitation potential. Both these parameters are dealt with in detail in Section 4.3 Chapter 4.

stoichiometric quantities; $[CO_3^{2-}]$ is estimated indirectly utilizing equilibrium chemistry of the carbonate system (discussed in detail in Chapter 4); $[Ca^{2+}]$ is measured directly by chemical means. The activity coefficient, f_D, can be calculated quite closely using the Debye-Huckel theory or some modification of this, see Eq (2.5) below; K_{sp} is determined from Eq (2.2).

<u>Calculation of the divalent ion activity coefficient</u>, f_D: In low salinity waters (TDS $\leqslant$ 4000 mg/ℓ) two factors principally affect f_D, electrostatic interactions between ions of opposite charge* and temperature.

Electrostatic effects: The activity coefficients for both divalent (f_D) and monovalent ions (f_m) are closely given by the Davies Equation,

$$\log f_i = -Az_i^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0{,}3.\mu\right) \tag{2.5}$$

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

A = temperature dependant constant

z_i = charge on species i, equal to 1 for mono and 2 for divalent ions.

μ = ionic strength

= $\frac{1}{2} \Sigma C_n z_i^2$

C_n = concentration of the n^{th} ion, moles/ℓ.

To calculate the ionic strength, μ, requires a complete chemical analysis of the water. Fortunately however, the activity coefficients, determined by Eq (2.5), are not very sensitive to ionic strength so that if only an approximate estimate of ionic strength is available, the activity coefficients can be determined with a degree of accuracy adequate for most water treatment problems. Langelier (1936) established experimentally that in most natural waters the ionic strength can be estimated sufficiently closely from the total inorganic dissolved solids concentration, S_D, as follows:

$$\mu \approx 2{,}5.10^{-5}\ S_D \tag{2.6}$$

where μ = ionic strength, moles/ℓ

S_D = total inorganic dissolved solids, mg/ℓ.

This relationship is adequate only for values of S_D up to 1000 mg/ℓ.

Temperature: The effect of temperature on f_D, for TDS $\leqslant$ 1000 mg/ℓ, this can be accommodated by adjusting the value of A in Eq (2.5) as follows:

---

* As the TDS increases in value above 4000 mg/ℓ, factors additional to electrostatic effects increasingly influence the activities of ions. These are ion pairing, ionic hydration, ion-ion interactions and others. Determination of activity coefficients in such solutions is discussed by Loewenthal and Marais (1984).

$$A = 1,825.10^6(78,3.T)^{-1,5} \qquad (2.7)$$

where T = Temperature in Kelvin (K).*

Knowing the value of K_{sp} (from Eq 2.2) and f_D at temperature T, the value of K'_{sp} is found from Eq (2.4).

Example: Determine pK'_{sp} for water with temperature 15°C and TDS = 160 mg/ℓ.
Calculation of K'_{sp} is carried out in three steps: (a) thermodynamic solubility product, K_{sp}, is determined at temperature 15°C from Eq (2.2), (b) divalent activity coefficient, f_D, is determined for TDS = 160 mg/ℓ and adjusted for a temperature of 15°C from Eqs (2.7 to 2.5), and (c) K'_{sp} is determined from Eq (2.4)

(a) Determine thermodynamic solublility product, K_{sp}:

Substituting T = 15°C into Eq (2.2),

$$pK_{sp} = 8,03 + 0,01183.(15,0)$$
$$= 8,21$$

i.e.

$$K_{sp} = 6,2.10^{-9}$$

(b) Determine divalent activity coefficient, f_D: The temperature effect on the activity coefficient is determined from the parameter 'A' via Eq (2.7), ionic strength, μ, is determined from TDS via Eq (2.6), thereafter the activity coefficient, f_D, is determined from Eq (2.5).

(i) Temperature effect on parameter A, from Eq (2.7) for T = (273 + 15) = 288 K,

$$A = 1,825.10^6(78,3.288)^{-1,5}$$
$$= 0,539$$

(ii) Ionic strength, μ, from Eq (2.6) for TDS = 160 mg/ℓ,

$$\mu = 2,5.10^{-5}(160)$$
$$= 0,004$$

Substituting A = 0,539 and μ = 0,004 into Eq (2.5) and solving for f_D,

---

* If TDS > 1000 mg/ℓ the effect of temperature on ionic behaviour still is not well understood and can be accommodated only approximately. In any event the simple equilibrium relationships set out here no longer are adequate at high TDS. A model for high salinity waters is available but is limited to 25°C. (Loewenthal and Marais, 1984).

$$\log f_D = -0,539(2)^2 \left\{\frac{0,004^{1/2}}{1 + 0,004^{1/2}} - 0,3.\ 0,004\right\}$$

$$= -0,126$$

i.e.

$$f_D = 0,75$$

(c) Apparent solubility product K'_{sp}, from Eq (2.4)

$$K'_{sp} = K_{sp}/f_D^2$$
$$= 6,2.10^{-9}/(0,75)^2$$
$$= 11,06.10^{-9}$$

i.e.

$$pK'_{sp} = -\log_{10}(K'_{sp}) = 7,96$$

2.2.2 Rates of dissolution and precipitation

The discussion in Section 2.2.1 only deals with the equilibrium saturation state of calcium carbonate in water; no information is given as to the rate at which saturation is attained and the variables which affect this rate.

The reactions between dissolved species of the carbonate system attain equilibrium virtually instantaneously; in contrast dissolution of solids and precipitation of solids out of solution are relatively slow processes. The more undersaturated a water, the higher the rate of dissolution of solid calcium carbonate. Similarly, the more supersaturated a water the higher the rate of precipitation of calcium carbonate out of solution.

The rate of precipitation, or conversely, of dissolution, has been modelled by Sturrock, Loewenthal and Marais (1976) to be of the form

$$-\frac{d[Ca^{2+}]}{dt} = k\ S\ f_D^2\ \{[Ca^{2+}]^{1/2}[CO_3^{2-}]^{1/2} - (K_{sp}/f_D^2)^{1/2}\}^2 \qquad (2.8a)$$

$$= kS\ \{(Ca^{2+})^{1/2}(CO_3^{2-})^{1/2} - K_{sp}^{1/2}\}^2 \qquad (2.8b)$$

where k = precipitation rate constant
S = surface area of calcium carbonate growth/dissolution sites
[ ] = concentration, moles/ℓ
( ) = activity, moles/ℓ.

Equation (2.8) has practical application in design of softening plants but for estimation of precipitation and dissolution rates in distribution systems it has value only in indicating qualitatively the expected rate of precipitation and dissolution, whether it be high or low, for the following reason: In Eq (2.8) the rate depends on the rate constant, k, the surface area of mineral growth/dissolution sites, S, and the term in brackets $\{(Ca^{2+})^{1/2}(CO_3^{2-})^{1/2} - K_{sp}^{1/2}\}^2$. The rate constant k is affected to some unknown degree by the crystal structure; the surface area of mineral growth/dissolution sites, S, depends on the size, mass and structure of crystals. Both k and S are unknown quantities in water distribution systems. The term in brackets is the only one that can be controlled in distribution systems; if it is small the degree of super- or undersaturation is small and the rate of precipitation or dissolution will be correspondingly low, and vice versa. Consequently, by limiting the degree of super- or undersaturation, the rate of precipitation or dissolution also will be limited. Insofar as the dissolution of calcium carbonate from cement and concrete type pipes is concerned, although it is desirable to have a water that is slightly supersaturated, if the water should be slightly undersaturated the drive for dissolution of the pipe walls will be small, and the rate of dissolution concomitantly low, in which event the life of the pipe might be affected only to a minor degree (see Section 2.2.4 of this chapter for discussion of the required state of supersaturation).

2.2.3 Effects of organics on precipitation and dissolution

The discussion so far has considered water which contains minimal dissolved organic material. In waters polluted with raw sewage or sewage effluents, and in waters having dissolved humic substances (the so-called "brown" waters) the presence of dissolved organic material causes a significant decrease in precipitation and dissolution rates. Considering precipitation, the rate decreases to zero, that is, precipitation apparently ceases, even though the molar product of the calcium $[Ca^{2+}]$ and carbonate $[CO_3^{2-}]$ species concentrations exceeds the apparent solubility product, K'_{sp}, (Eq 2.4), by an order of magnitude or more (i.e. pK'_{sp} apparently decreases by more than one logarithmic unit). Conversely, considering dissolution of solid calcium carbonate, dissolution apparently ceases even though the species molar product is significantly less than the apparent solubility product, K'_{sp}, as determined from Eq (2.4) (i.e. pK'_{sp} apparently increases). That is, calcium carbonate precipitation and dissolution reactions in water containing dissolved organics stop short of thermodynamic equilibrium. This phenomenon is depicted graphically in Fig 2.1 in which the precipitation/dissolution rate is plotted versus the logarithm of the product of calcium and carbonate species concentrations; for precipitation and dissolution reactions the rate is virtually zero at $-\log([Ca^{2+}][CO_3^{2-}])$ values well below, and well above, pK'_{sp} respectively. No unequivocal conclusions have been formed as to the causes of this behaviour. It is possible that certain dissolved organic materials are adsorbed onto crystal precipitation/dissolution sites to decrease reaction rates. These retardation effects have been encountered elsewhere in chemical reaction kinetics and Levenspiel (1962) suggests that these can, on occasion, be adequately modelled by introducing retardation precipitation and dissolution constants into Eq (2.8a). The precipitation/dissolution rate equation then is modified to

$$\frac{-d[Ca2+]}{dt} = k\ S\ f_D^2\ [\{[Ca^{2+}]^{1/2}[CO_3^{2-}]^{1/2} - K'_{sp}\}^2 - \{[Ca^{2+}]_z^{1/2}[CO_3^{2-}]_z^{1/2} - K'_{sp}\}^2] \qquad (2.8c)$$

where $[Ca^{2+}]_z.[CO_3^{2-}]_z$ = retardation constant equal to the product of concentrations of calcium and carbonate species when the measured precipitation or dissolution rate is, to all intents and purposes, zero. This product constant is determined by experiment for a particular water.

An alternative approach to precipitation of calcium carbonate from waters containing dissolved organics has been to model the state of supersaturation (i.e. precipitation phenomena) relative to an 'ionic product precipitation constant' determined experimentally for each water (Wiechers, 1978). The value for the constant is found as follows:

> The product of the concentrations of calcium and carbonate species when the measured precipitation rate is to all intents and purposes zero, is taken as the value for this constant, i.e.

When $-d[Ca^{2+}]/dt = 0$,

$[Ca^{2+}][CO_3^{2-}]$ = ionic product precipitation (IPP) constant
$= K_{IPP}$
$= [Ca^{2+}]_z.[CO_3^{2-}]_z$ in Eq (2.8c)

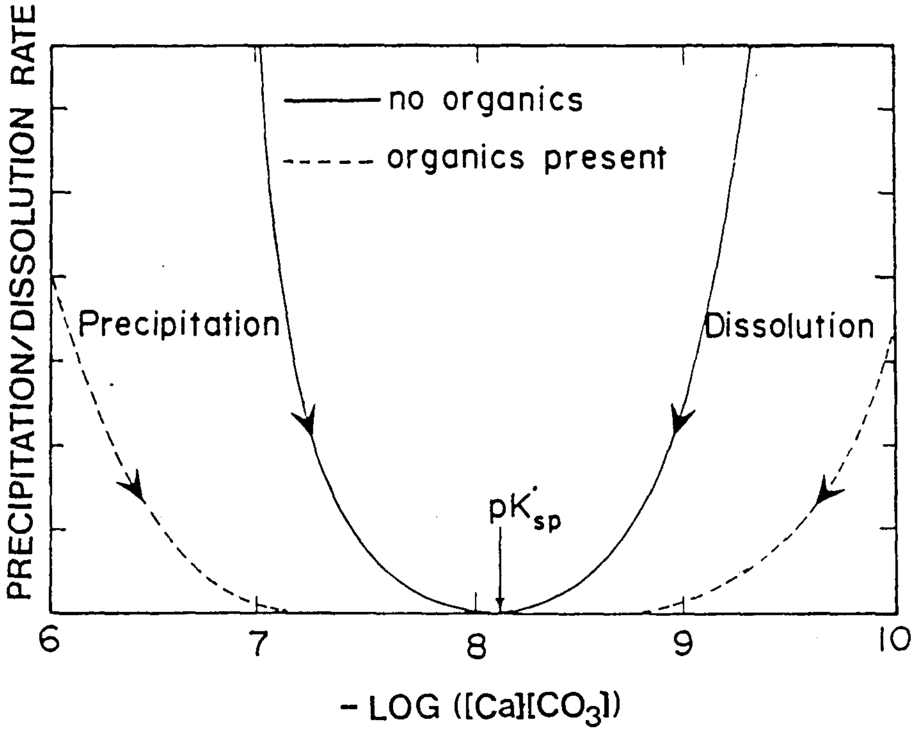

Fig 2.1 Calcium carbonate precipitation and dissolution rates in water with and without dissolved organic material using Eq 2.8c. (Arrows indicate the direction of reaction)

It should be noted that the constant, K_{IPP}, is neither a thermodynamic nor apparent thermodynamic constant, but a pseudo constant, because its value will differ depending on whether K_{IPP} is determined from precipitation or dissolution experiments.

Values for the ionic product precipitation constant, K_{IPP}, for various effluents in the high lime water reclamation process have been reported by Merrill and Jorden (1974) and Wiechers (1977,1978); these are listed in Table 2.1 below.

By following an analogous approach, values for ionic product dissolution (IDP) constants, K_{IPD}, can be determined, but no work on this aspect appears to have been done.

The discussion above has two important consequences relevant to chemical treatment of waters, in (1) high lime water reclamation, (2) transportation and storage of soft 'brown' waters.

(1) High lime water reclamation: For water softening in the high lime water reclamation process, lime dosages will be significantly higher than dosages required to attain the same degree of softening for waters without dissolved organics (see Chapter 5 for softening calculations). If an effluent from a high lime treatment process is passed through activated carbon columns to reduce organic material to trace values, the ionic product precipitation constant (with a pseudo pK_{IPP} value of about 7) reverts to the apparent solubility product value with a pK'_{sp} value of about 8. Consequently, a water after the high lime treatment process which is apparently saturated, or even undersaturated, relative to pK_{IPP}, may after carbon filtration become supersaturated (relative to pK'_{sp}) and give rise to precipitation and scaling problems.

(2) Transport and containment of soft brown waters: Surface waters, for example those from the Table Mountain sandstone regions, in the south western, southern and south eastern regions of Southern Africa, usually have a low pH (pH < 6) and are highly coloured due to dissolved humic substances. These substances, although organic, are virtually inert biologically and do not constitute pollution in the normal understanding of this word. When assessed in terms of their degree of undersaturation with respect to K'_{sp}, these waters should be grossly aggressive to cement and concrete lined conduits. However, the presence of the humic substances appears to induce a pseudo ionic product dissolution constant very much smaller than K_{sp} (i.e. $pK_{IPD} > pK_{sp}$) so that dissolution of the calcium carbonate from the cement matrix does not occur.

The composition of the humic substances in these brown waters varies widely and no information base has been established that quantitatively relates the humic composition with the degree of protection afforded. It is likely that many brown waters can be transported in pipes of cement material or stored in cement lined structures without resulting aggression; if the humic content is small aggression in some degree can be anticipated; if none is present, as in waters derived from snow melts, aggression is very likely. In all events such waters should be tested for aggressive behaviour. The simplest test in this regard is the Marble Test (see Standard Methods, 1985) to determine whether dissolution of calcium carbonate minerals is likely or not.

In an analogous fashion that saturated high lime treated effluents become supersaturated after activated carbon treatment, so non-aggressive brown waters become grossly aggressive after colour removal. This point has not always been appreciated, that when colour has been removed from surface waters, for example those from the Table Mountain sandstone series, they become very aggressive. This effect has been implicated as the cause for structural failures of asbestos cement piping and concrete reservoirs. Chemical treatment of these waters after colour removal, to make them non-aggressive (stable), is imperative if deterioration of concrete and cement material is to be arrested. Procedures for stabilization are set out in Chapter 5.

Table 2.1. Experimental apparent ionic product precipitation constant values for various lime treated waters and effluents at about 25°C. (The thermodynamic solubility product constant for this temperature is pK_{sp} = 8,32, Truesdell and Jones, 1973).

Water and Effluent type	pK_{IPP}^{*}
Merrill and Jorden (1974)	
Well water	7,4
Primary and secondary effluent	6,7
Raw waste	6,4
Anaerobic digester supernatant	6,3
Wiechers (1977)	
Primary	6,8
Secondary Recarbonated	7,4

* $pK_{IPP} = -\log([Ca^{2+}][CO_3^{2-}])$ at zero precipitation rate

2.2.4 Supersaturation requirements for non-aggression

When a water is distributed in a reticulation system comprised wholly of concrete and/or asbestos cement pipes, then if the water is saturated with respect to calcium carbonate at the entry to the system it will remain so, or it will become supersaturated (due to any dissolution of $Ca(OH)_2$ in the concrete) provided there is no generation of carbon dioxide from biological activity in the system. To guard against the development of undersaturated conditions from carbon dioxide generation, a slight degree of supersaturation is desirable, a calcium carbonate precipitation potential* of 1 to 2 mg/ℓ is recommended.

Where reticulation systems include cast iron or mild steel conduits, it will be shown in Chapter 3 that it is insufficient to specify a precipitation potential as the sole criterion to guard against metal corrosion - additional criteria, which include minimum concentrations of calcium and carbonate species, need to be satisfied; moreover corrosion reactions reduce the degree of supersaturation. For these reasons when metal and cement conduits are used in a reticulated system the degree of supersaturation should be higher than that recommended above for concrete and asbestos cement conduits only. Exactly what it should be cannot be stated unequivocably, one can only refer to distribution systems that contain both types of conduits where the indications are that the imposed degree of supersaturation appears to have controlled aggression. One example, where corrosion appears to be controlled, is the city of Cape Town reticulation system where the treatment is such that a precipitation

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* The calcium carbonate precipitation potential is the mass concentration of $CaCO_3$ that can be precipitated by a supersaturated water to reach saturation. This parameter, and quantitative assessment of it, is discussed in detail in Chapters 4 and 5.

potential of about 4mg/ℓ $CaCO_3$ is provided prior to distribution.*

The concept of a precipitation potential is well appreciated in terms of the Marble test, but has not found application as a control parameter in water treatment because no simple method has been available whereby the potential can be determined from the measurements normally done to control water quality (i.e. pH, Alkalinity and calcium content). In part also the precipitation potential approach has been neglected because assessment of the saturation state, via the Langelier and Ryznar Indices, has attained general acceptance - it has been presumed that if, for example, the Langelier Index for a water is positive (equal to about +0,2) the water will be non-aggressive. However, in Chapter 4 it shall be shown that for the same Langelier Index, of say +0,2, one water can have a precipitation potential of 20 mg/ℓ $CaCO_3$ and another only 2 mg/ℓ, - the index gives no consistent quantitative description of the degree of super- (or under-) saturation. Langelier (1936), recognized this deficiency - he stated "It should be emphasized that the Saturation Index is an indication of directional tendency and of driving force but that it is in no way a measure of capacity".

Calculation of the precipitation potential using the equilibrium equations is tedious and not suitable for routine control purposes. However, with the development of conditioning diagrams, see Chapters 4 and 5, the precipitation potential is determined as easily as the Langelier Index. Furthermore, the chemical dosing requirements to impose the desired potential are calculated very simply. Thus, although no firm conclusions can be stated regarding a desirable value for the precipitation potential, substitution of the potential for the Langelier index as the saturation reference parameter will, in our opinion, rationalize the comparative aggressiveness or non-aggressiveness of different waters.

In the absence of a data base on the precipitation potential, but taking due cognisance of the range of potentials possible for a Langelier Index of +0,2, it would seem that a precipitation potential of 4 to 6 mg/ℓ (as $CaCO_3$) is a reasonable value.

2.3 AGGRESSION DUE TO HIGH SULPHATE CONTENT

Dissolved sulphate species have an adverse effect on cement type materials. Waters containing over about 350 mg/ℓ SO_4^{2-} have been found to be aggressive to ordinary Portland cement. Lea (1949, 1956) identifies three modes of attack (see Fulton 1977 and van Aardt and Fulton, 1977):

(i) Hydrated calcium aluminates and ferrites in the cement can be converted to calcium sulpho-aluminates and sulpho-ferrites. These compounds occupy a greater volume than the original hydrates and their formation can lead to disintegration of the concrete.

(ii) Calcium hydroxide in the set cement can be converted to calcium sulphate; crystal formation of this mineral within the cement also can lead to disintegration of the cement as a result of the expansion of the reaction products.

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* This precipitation potential is calculated from measured data for Alkalinity, pH and calcium concentration of the treated water prior to distribution (see Chapter 5).

(iii) Decomposition of hydrated calcium silicate within the cement can take place, which reduces the strength of this material.

The modes of attack listed above depend on cation species in the principal ionic matrix. Where Mg^{2+} is the principal cation any or all of (i), (ii) and (iii) can occur; where Na^{+} is the principal cation, only(i) or/and (ii), and where Ca^{2+} is the principal cation only (i).

Cement and concrete with the following specific chemical and physical properties, have an increased resistance to sulphate attack, Fulton (1977):

(i) Cements: A low content of tricalcium aluminate in the cement paste, less than about 5,5 percent, affords virtually complete protection to sulphate attack.

(ii) Concrete: A high mass of cement per cubic metre of concrete, of approximately 400 kg cement/m^3, provides increased resistance to sulphate attack. Lean mixes of less than 310 kg cement/m^3 are particularly vulnerable to attack.

2.4 TENTATIVE GUIDELINES FOR THE PREVENTION OF AGGRESSION OF WATER TO CEMENT AND CONCRETE

In the above sections the water quality factors that influence water's aggression to cement and concrete surfaces and precipitation on such surfaces have been discussed. Based on this information the following guidelines are proposed whereby aggression and deposition can be controlled:

Guideline 1: The chemical state of the water needs to be adjusted to a slight state of supersaturation with respect to calcium carbonate: a precipitation potential of about 4 mg/ℓ is recommended. For waters containing significant dissolved organic compounds, for example the soft brown waters of the Western Cape, this guideline may be unduly stringent. Experience from a number of these waters indicates a decrease in aggression due to the presence of dissolved humic substances. However, it has not been established whether this observation is general, and, how this ameliorating effect varies with dissolved humic substance concentration. It should be noted that these soft waters, unless appropriately stabilized, are likely to be corrosive in some degree to metal pipes and fittings (see Chapters 3 and 5).

Guideline 2: For waters with sulphate content in excess of 350 mg/ℓ (as SO_4^{2-}), the cement material used in the manufacture of both asbestos cement and concrete should have a tricalcium aluminate content of less than 5,5 percent. Furthermore, for concrete pipes and structures conveying and containing such waters the cement content should be in excess of 400 kg cement per cubic metre of concrete.

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Chapter 3

Corrosion and Passivation

3.1 INTRODUCTION

The conduit material in municipal water reticulation systems (excluding household connections) usually will be of cement, concrete, cast iron, mild steel and plastics. In this chapter we shall consider corrosion, and passivation of ferrous metals such as cast-iron and mild steel.

Corrosion of the metal components of pipes carrying water is the result of oxidation and reduction reactions at sites on the metal-water interface, by the formation of electro-chemical cells each with an anodic and cathodic area, see Fig 3.1. At the anode metal molecules lose electrons to form metal ions which pass into solution: At the cathode the electrons (generated at the anode) pass from the metal (electron donor) to some chemical species (electron acceptor) in the water adjacent to the cathode; this is usually molecularly dissolved oxygen, if present. These reactions induce significant changes in the chemical composition of the water adjacent to the anodic and cathodic areas. Depending on the circumstances, the reactions may cause continuous dissolution of the metal into the water at the anode (corrosion), or, may give rise to precipitation of minerals over the anode and cathode thereby reducing the areas of the active electro-chemical sites, and the rates of the reactions eventually stopping the corrosion completely (passivation of the surface).

To understand the mechanism of corrosion and of passivation through the formation of oxide scales, it is necessary to review the various redox reactions and their consequences at the anode and cathode.

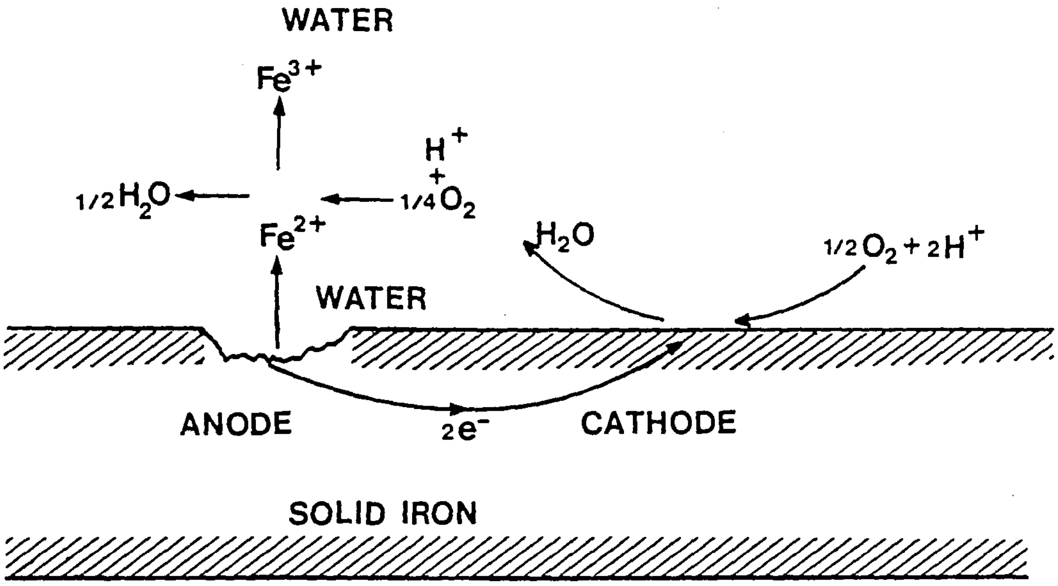

Fig 3.1 Fundamental corrosion reactions for cast iron and mild steel pipes transporting municipal water.

3.2 CORROSION REACTIONS

3.2.1 Anodic Reactions

At the anode metal ions go into solution in the least oxidized dissolved form (Fe^{2+} for mild steel and cast iron), by oxidation of the solid iron, Fe_s,

$$Fe_{(s)} \rightarrow Fe^{2+} + 2e^- \qquad (3.\ 1)$$

This reaction is the primary level corrosion reaction for iron. Thereafter, at the anode surface, there are alternative pathways of secondary and tertiary reactions, the specific pathway depending on the chemical composition of the water above the anode and the relative rates of the reactions at the secondary and tertiary levels (see Fig 3.2).

Secondary level anodic reactions: The various possible secondary level reactions between Fe^{2+} and the species in solution are as follows:

(i) The Fe^{2+} can precipitate in two ways, as $Fe(OH)_2$ and/or, as $FeCO_3$ (siderite) the latter when carbonate species are present in the water, i.e.

$$Fe^{2+} + 2\ H_2O \rightarrow Fe(OH)_2 \downarrow + 2H^+ \qquad (3.\ 2)$$

and/or

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \downarrow \qquad (3.\ 3)$$

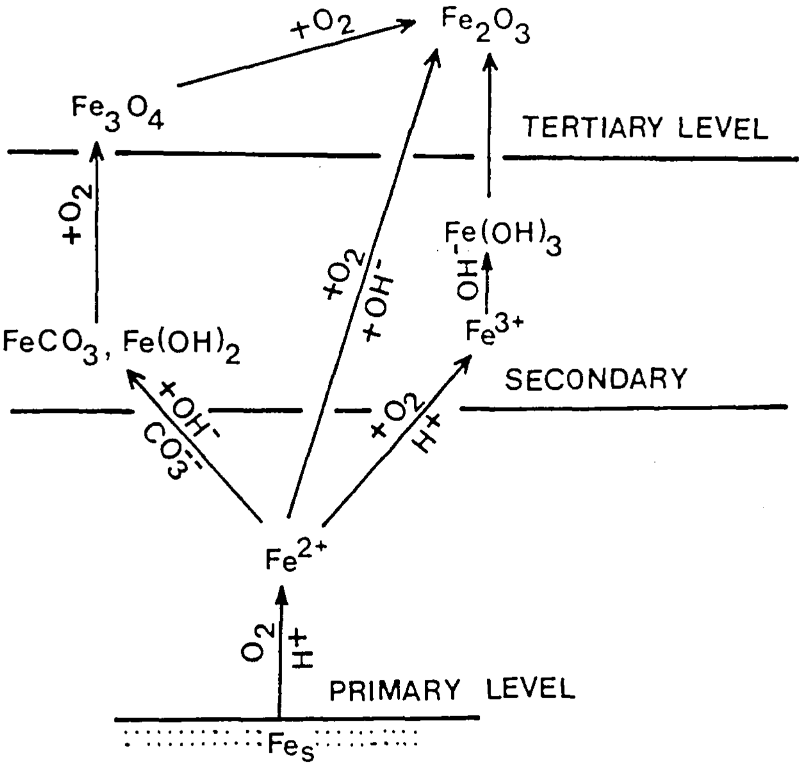

Fig 3.2 Anodic reaction pathways for iron in contact with oxygenated water containing carbonate species.

There is no electron transfer in either of these reactions so that these can take place whether oxygen is present in the water above the anode or not.

(ii) If oxygen is present above the anode, then an alternative reaction is possible at the secondary level, the oxidation of Fe^{2+} to Fe^{3+},

$$Fe^{2+} + \tfrac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2} H_2O \qquad (3.4a)$$

The Fe^{3+} formed in the above reaction is then precipitated as $Fe(OH)_3$,

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_{3(s)} \downarrow + 3H^+ \qquad (3.4b)$$

Of these two reactions the formation of $Fe(OH)_3$ from Fe^{3+} is rapid compared with the rate of formation of Fe^{3+} from Fe^{2+}.

Summing the above two reactions, Eqs (3.4a and 3.4b), the overall reaction for precipitation of $Fe(OH)_3$ at the secondary reaction level is

$$Fe^{2+} + \tfrac{1}{4} O_2 + \tfrac{5}{2} H_2O \rightarrow Fe(OH)_{3(s)} + 2H^+ \qquad (3.5)$$

The precipitates $Fe(OH)_2$ and $Fe(OH)_3$ are transient metastable solid states and exist, therefore, only as "fresh" precipitates. Both are precursors to the thermodynamically stable iron oxides (see next section on tertiary level reactions). That is, the fresh precipitates $Fe(OH)_2$ and $Fe(OH)_3$ exist in a pseudo equilibrium state with respect to the dissolved species.

The potential for the secondary level reactions described above is best illustrated by means of a Pourbaix diagram, also known as a pe-pH diagram (Wahed and Pourbaix, 1954). In this diagram the axes are redox potential, plotted as the negative logarithm of the electron activity (pe), and pH; lines can be drawn depicting selected partial pressures of oxygen, $\bar{p}O_2$, at equilibrium with the water species, i.e. pe, pH and $\bar{p}O_2$ are linked by an equilibrium relationship. If an iron salt is dissolved in the water the relative concentrations of iron species Fe^{2+} and Fe^{3+} will depend on the redox potential. With regard to solid precipitates, the various iron minerals expected to form will depend on both pH and redox potential (or one of these and $\bar{p}O_2$). By utilizing equilibrium relationships between the species one can define regions in which particular dissolved species and mineral precipitates will be dominant. Procedures to construct this type of diagram are set out in detail by Garrels and Christ, (1965). Figure 3.3 illustrates such a pe-pH diagram for the metastable products in a water with total dissolved iron concentration, Fe_T, of 10^{-5}moles/ℓ and total carbonate species concentration, C_T, of 10^{-3}moles/ℓ and two selected oxygen partial pressures.

Referring to Fig 3.3, from a pseudo-equilibrium point of view, for partial pressures of oxygen down to about 10^{-60} atmospheres* the metastable solid is $Fe(OH)_3$. If the

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*Water in equilibrium with air at S.T.P. has a partial pressure of oxygen of 0,2 atmospheres and concentration of 8,2 mgO/ℓ.

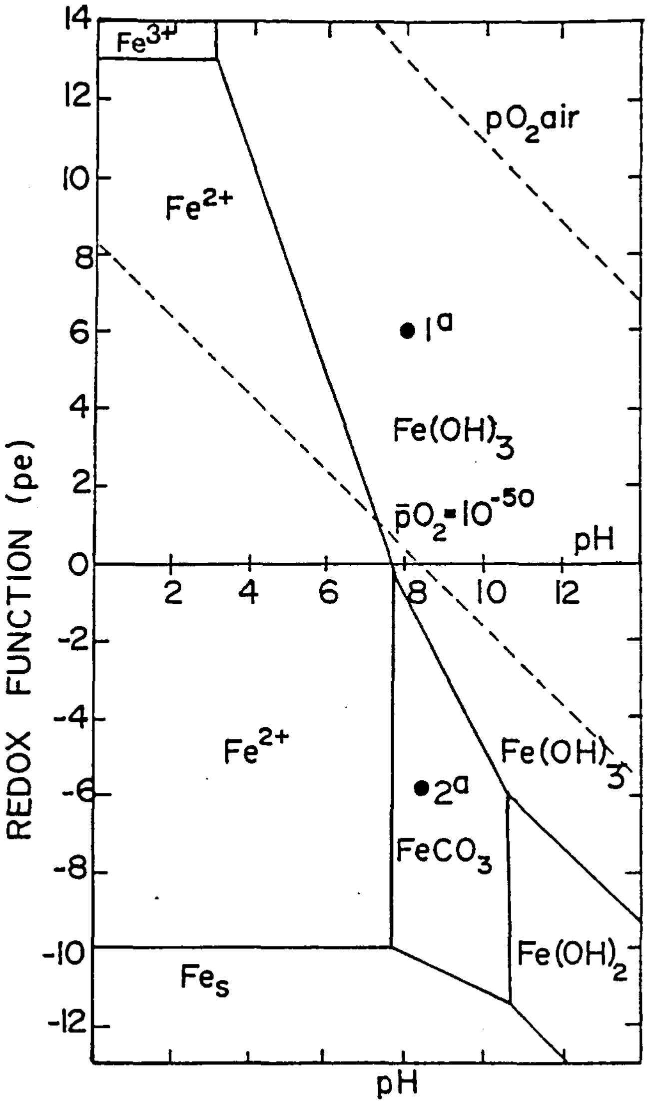


Fig 3.3 pe-pH diagram for metastable equilibrium of the iron-carbonate-water system; $Fe_T = 10^{-5}$ moles/ℓ, $C_T = 10^{-3}$ moles/ℓ and temperature 25°C.

partial pressure of oxygen is less, the metastable solid is either $FeCO_3$ or $Fe(OH)_2$ depending on pH, C_T and Fe_T. An important point to note here is that even if $Fe(OH)_3$ is the metastable solid, the minerals $Fe(OH)_2$ and $FeCO_3$ also can precipitate, however, with time, these two minerals should transform to either the metastable $Fe(OH)_3$ or the stable γFe_2O_3 (see tertiary level reactions). Evidently a mixture of minerals can be present at any time. The relative masses of each cannot be predicted by the equilibrium or pseudo equilibrium equations; the relative masses of mineral present are functions of the rates of formation of the metastable and final products and the sequence in which the products are formed.

Tertiary level anodic reactions: The thermodynamically stable corrosion products which might form over the anode from the metastable reactants $Fe(OH)_2$,$Fe(OH)_3$ and $FeCO_3$ are the oxides haematite, γFe_2O_3, and magnetite, Fe_3O_4. In Fig. 3.4 a Pourbaix diagram for the thermodynamically stable reactants and products is shown. The potential for occurrence of the products depends primarily on the redox potential (pe) and the pH of the water adjacent to the anode. The Pourbaix diagrams, Figs 3.3 and 3.4, therefore show the secondary and tertiary level product regions respectively, the chemical state of a water plotting at a point in each of the diagrams, each point being defined by a particular pH and pe value (or an equivalent $\bar{p}O_2$ value). Any two of the three parameters pe, pH and $\bar{p}O_2$ are sufficient to establish the chemical condition. For example, if the pe and pH adjacent to the anode are +6,0 and 8,0 respectively, then in Fig 3.3 the state plots at Point 1a in the region of the metastable solid for metastable equilibrium of $Fe(OH)_3$, and, in Fig 3.4 in the region of the stable solid haematite, γFe_2O_3. Similarly, if the pe and pH are -6,0 and 8,4 respectively, then in Fig 3.3 the state point plots at Point 2a in the region of the metastable solid $FeCO_3$, and, in Fig 3.4 in the region of the stable solid magnetite, Fe_3O_4. It is important to note that the reactions are relevant to pseudo equilibrium and equilibrium states only. No consideration is given to either the mechanism of formation of the various solid phases or the kinetics of formation of reactants and products, or, the mass concentrations of minerals formed.

The various possible tertiary level anodic reactions that might take place, to transform the secondary level products, $Fe(OH)_3$, $Fe(OH)_2$ and $FeCO_3$ (in Fig 3.3) to the stable oxides Fe_2O_3 and Fe_3O_4 (Fig 3.4), are as follows:

(i) The metastable mineral reactant $Fe(OH)_3$, which only forms if oxygen (or an alternative electron acceptor) is present, is transformed in time to stable haematite, γFe_2O_3,

$$2\ Fe(OH)_{3(s)} \rightarrow \gamma Fe_2O_{3(s)} + 3H_2O \qquad (3.\ 6)$$

(ii) The metastable reactant $Fe(OH)_2$, if oxygen is present, may be oxidized to haematite, γFe_2O_3, via magnetite, Fe_3O_4 (Feitknecht, 1959).

For Fe_3O_4 formation,

$$6\ Fe(OH)_{2(s)} + O_2 \rightarrow 2Fe_3O_{4(s)} + 6\ H_2O \qquad (3.7a)$$

and for γFe_2O_3 formation, by further oxidation of Fe_3O_4,

$$2\ Fe_3O_{4(s)} + \tfrac{1}{2}\ O_2 \rightarrow 3\ \gamma Fe_2O_{3(s)} \qquad (3.7b)$$

The overall reaction for the formation of γFe_2O_3 from $Fe(OH)_2$ is given by the sum of the reactions in Eqs (3.7a and 3.7b),

$$6\ Fe(OH)_{2(s)} + \frac{3}{2}\ O_2 \rightarrow 3\ \gamma Fe_2O_{3(s)} + 6\ H_2O \qquad (3.\ 8)$$

(iii) The reactant $FeCO_3$, if oxygen is present, may be oxidized to either goethite, FeOOH (Sontheimer, Kolle and Snoeyink, 1981) or to haematite, γFe_2O_3 via magnetite, Fe_3O_4, (Sontheimer <u>et al.</u>, 1981, and Feitknecht, 1959). For goethite formation,

$$2\ FeCO_{3(s)} + \tfrac{1}{2}\ O_2 + H_2O \rightarrow 2\ FeOOH_{(s)} + 2\ CO_2 \qquad (3.\ 9)$$

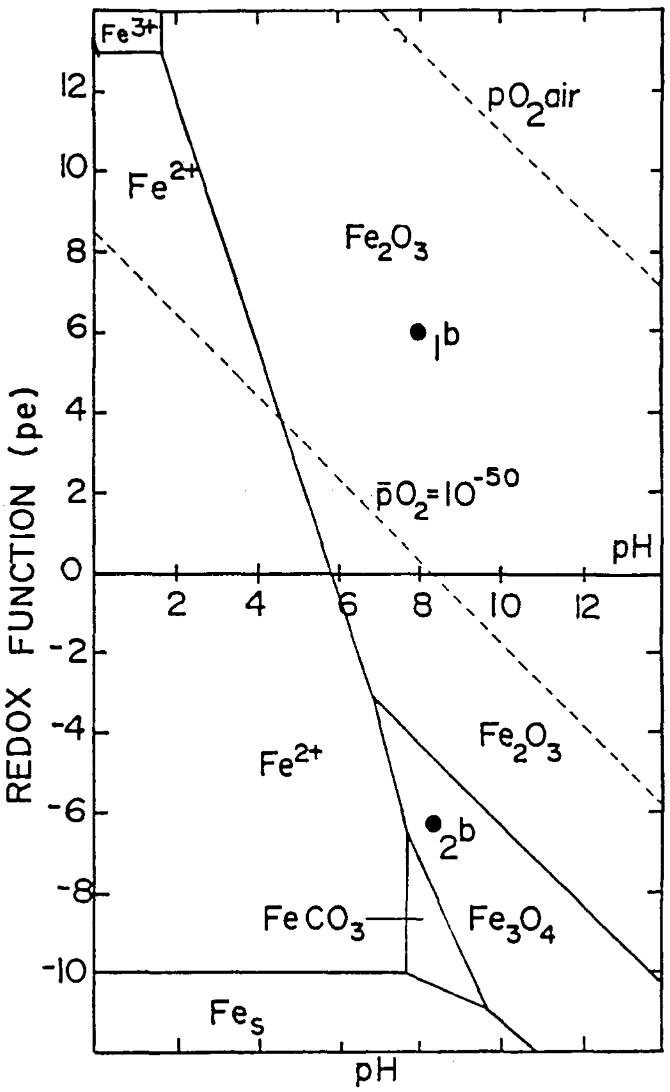


Fig 3.4 pe-pH diagram for equilibrium of the iron-water-carbonate system; $Fe_T = 10^{-5}$ moles/ℓ, $C_T = 10^{-3}$ moles/ℓ and temperature 25°C.

For magnetite formation,

$$3\ FeCO_{3(s)} + \tfrac{1}{2}\,O_2 \rightarrow Fe_3O_{4(s)} + 3\ CO_2 \qquad (3.10)$$

and, for the conversion of magnetite to haematite,

$$2\ Fe_3O_{4(s)} + \tfrac{1}{2}\,O_2 \rightarrow 3\ \gamma Fe_2O_{3(s)} \qquad (3.11)$$

(iv) The reactant Fe^{2+}, if oxygen and water are present, may be oxidized directly to magnetite and/or haematite on the anode surface. For magnetite formation,

$$3\ Fe^{2+} + \tfrac{1}{2}\,O_2 + 3\ H_2O \rightarrow Fe_3O_{4(S)} + 6H^+ \qquad (3.12)$$

For haematite formation,

$$2\ Fe^{2+} + \tfrac{1}{2}O_2 + 2\ H_2O \rightarrow Fe_2O_{3(s)} + 4H^+ \qquad (3.13)$$

With the reactions above, as illustrated in Fig 3.4, for the concentrations of oxygen usually found in a water distribution system, $O_2 > 1$ mg/ℓ, the stable end products are goethite, FeOOH, or haematite, γFe_2O_3. If oxygen is present only at extremely low concentrations the stable end products are likely to be siderite, $FeCO_3$, or magnetite, Fe_3O_4.

From the description of product formation in the various reaction pathways, a number of minerals may form above the anode (i) secondary products $Fe(OH)_2$, $FeCO_3$ and $Fe(OH)_3$, and (ii) tertiary products γFe_2O_3, FeOOH and Fe_3O_4. Secondary product deposits are porous and have very little effect on the anodic reaction rate, but tertiary products tend to be dense and inert and reduce the reaction rate. If tertiary product formation is achieved over the anodic areas it will eventually terminate the corrosion reaction (Stumm 1960; Sontheimer et al., 1981; Kolle and Rosche, 1980). Tertiary product film formation however will not take place if the rate of formation of secondary products exceeds the rate of formation of tertiary products, a situation manifested either by 'red water' discharge from the pipe or 'tubercule' formation in the pipe system. Red water formation usually is found with water having pH $\lesssim$ 7 and tubercule formation with water having pH $\gtrsim$ 7,5. Stumm and Morgan (1970) describe the occurrence of these two phenomena as follows:

> The rate of oxidation of Fe^{2+} to Fe^{3+} in oxygenated water (without organics) depends on pH and the partial pressure of dissolved oxygen as follows:
>
> $$-\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}]\ 10^{2pH}.\ \bar{p}O_2 = +\frac{d[Fe^{3+}]}{dt} \qquad (3.14)$$
>
> where k = rate constant
> $\bar{p}O_2$ = partial pressure of dissolved oxygen in atmospheres.
> $[Fe^{2+}]$ = ferrous ion concentration in moles/ℓ.
>
> Fe^{2+} is generated at the anode as described by Eq (3.1). Equation (3.14) indicates that for pH < 7 the rate of oxidation of Fe^{2+} to Fe^{3+} is slow so that most of the Fe^{2+} passes through the monolayer, at the interface between the metal and the water, into the bulk solution before oxidation to Fe^{3+}. When Fe^{2+} is oxidized to Fe^{3+} in the bulk solution the secondary and tertiary products are precipitated in a finely dispersed form to give rise to 'red water' formation. If the pH is high, then, from Eq (3.14), oxidation rate of Fe^{2+} to Fe^{3+} is rapid and consequently most of the oxidation occurs in the monolayer; secondary products precipitate within the monolayer onto the surface as porous deposits in the form of tubercules. Subsequently the secondary products are oxidized to tertiary products but the tubercule formation is not disturbed. These tubercules do not form an effective seal because they are porous so that corrosion continues. Thus, the absence of red water is no guarantee that pacification has been achieved.

From the description above it would seem as if anodic passivation cannot be attained via the phenomena described. The crux of the problem lies in the rate of formation of Fe^{2+} (Eq 3.1); this rate is determined initially by the reactions at the cathode. If the cathodic reaction rates can be reduced to the extent that Fe^{2+} formation is so slow that the tertiary product formation at the anode can take place at the same rate as the secondary product formation then the tertiary products form on the surface as a dense film. It is necessary therefore to consider the cathodic reactions.

3.2.2 Cathodic Reactions

At the cathode some species (usually molecularly dissolved oxygen) act as acceptors of the electrons generated at the anode (see Eq 3.1). When oxygen is the electron acceptor, the cathodic reaction is

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (3.15)$$

The overall corrosion reaction is the sum of the two half reactions, the anodic reaction, Eq (3.1), and the cathodic reaction, Eq (3.15), i.e.

$$Fe_{(s)} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O \qquad (3.16)$$

The rate of the overall corrosion reaction, Eq (3.16), is governed by the slower of the two half reactions. The manner in which these two half reactions control corrosion becomes evident by considering a pure water and one containing carbonate and calcium species.

In pure water, containing dissolved oxygen, the corrosion rate usually is governed by the rate of oxygen supply to the cathode, and the corrosion rate is said to be cathodically controlled. In such a water it is not possible to obtain corrosion protection by oxide film formation for the following reasons: Where oxygen supply to the electrodes is low (due to a low oxygen level in the bulk water or/and poor mixing conditions), the cathodic reaction rate accordingly is slow, and hence also the anodic reaction rate, i.e. the rate of $Fe(OH)_2$ formation is slow. However, at such low oxygen tensions the rate of oxidation of $Fe(OH)_2$ to the iron oxides, see Eqs (3.6 to 3.13) tends to be even slower so that $Fe(OH)_2$ continuously displaces the oxides from the metal surface and an oxide film has no opportunity to form. Where the oxygen supply is high, $Fe(OH)_2$ and $Fe(OH)_3$ formation will be so rapid that the tertiary products cannot form against the anodic surface, and red water or tubercule formation will occur at low and high pH respectively as described previously and the corrosion surface is not passivated.

In waters containing calcium and carbonate species (and oxygen), the abstraction of H^+ from the water over the cathode, Eq (3.15), causes the pH to rise thereby increasing the CO_3^{2-} concentration. If the $CaCO_3$ solubility product is exceeded, precipitation of $CaCO_3$ takes place over the cathodic area reducing its effective size. The precipitate that forms over this area is permeable to a degree that depends on the nature of the precipitate, so that although the rate of the cathodic reaction is reduced, it is not completely terminated (Stumm, 1960). However, if this rate is reduced to such an extent that tertiary oxide formation on the anode surface can take place, in due course the anode becomes completely covered and the corrosion is terminated. Complete passivation, therefore, can occur only if the cathodically controlled corrosion rate at some stage is reduced sufficiently to allow tertiary oxide film formation on the anode; thereafter, if the anodic area is reduced sufficiently to commence controlling the corrosion rate, passivation goes to completion by anodic control.

The problem in ensuring passivation is to delineate the conditions in the water that will cause the cathodic rate to be reduced with time (via $CaCO_3$ precipitation) to such an extent that tertiary oxide film formation over the anode is possible. Solution to this problem requires enquiring into the factors affecting the nature (porosity) of $CaCO_3$ precipitate on the cathode: If the rate of $CaCO_3$ precipitation onto the cathode is fast, the precipitate is colloidal or microcrystalline in composition; if the rate is slow, well defined calcite crystals are formed. According to McCauley (1960), macrocrystalline precipitation onto the cathode tends to occur as a thin layer over the complete cathode surface forming a relatively dense and very nearly impermeable layer; when sufficient mass has precipitated it can reduce the overall corrosion rate to below the limiting value required for oxide film formation on the anode. In contrast, discrete crystal formation is relatively porous and permeable and does not slow down the cathodic reaction rate sufficiently for anodic oxide film formation to occur. Clearly, for optimal progress to passivation, the rate of precipitation onto the cathode surface must be as rapid as possible particularly after a new pipe has been put into operation.

Evidently, the rate of $CaCO_3$ precipitation over the cathodic areas is crucial in providing the appropriate conditions for passivation and merits further discussion. An equation modelling the rate of precipitation of $CaCO_3$ from the bulk solution onto a $CaCO_3$ surface has been set out in Chapter 2, Eq (2.8). It should be noted that this equation models a reaction between species in the bulk solution and the crystal layer being formed. However, immediately over the cathode additional factors (to be discussed later) usually cause the chemical state to differ significantly from that in the bulk liquid. However, the precipitation rate at the cathode surface is still governed by Eq (2.8) except that the chemical state is that in the adjacent water layer, i.e.

$$\frac{-d[Ca^{2+}]}{dt} = k\ S\ f_D^2\ \{[Ca^{2+}]_c^{1/2}\,[CO_3^{2-}]_c^{1/2} - K_{sp}^{1/2}/f_D\}^2 \qquad (3.17)$$

where $[\,]$ = concentration, moles/ℓ in the monolayer
k = rate constant
f_D = activity coefficient in the monolayer for divalent ions
subscript 'c' = value for the chemical parameter in the mono layer adjacent to the cathode.

The analysis above sets out the various reactions that can take place at the anode and cathode and the chemical products that can be formed. For passivation to occur the conditions in the monolayer above the anode and cathode must be favourable for both the formation and rates of formation of the desired end products. The problem is that conditions in the monolayer cannot be quantified rigorously from the conditions in the bulk liquid. Accordingly one must examine quantitatively various factors pertinent to the bulk liquid that affect conditions in the monolayer and endeavour to identify situations in the bulk liquid that tend to promote the conditions in the monolayer that favour passivation.

3.3 VARIABLES AFFECTING CORROSION AND PASSIVATION

Variables in the bulk liquid affecting the corrosion rate and passivation include, (i) dissolved oxygen concentration, (ii) velocity of flow, (iii) calcium and/or carbonate species concentrations and pH, (iv) buffer capacity, (v) presence of certain organic substances and (vi) concentrations of chlorides and sulphates. The influence of some of these factors on corrosion was determined experimentally by using the coupon test procedure set out by Stumm (1960); the effects of the remainder were assessed from reported literature. In all the tests black cast iron was used to give an indication of the expected trends of corrosion and passivation.The effects of each of the factors can be described as follows:

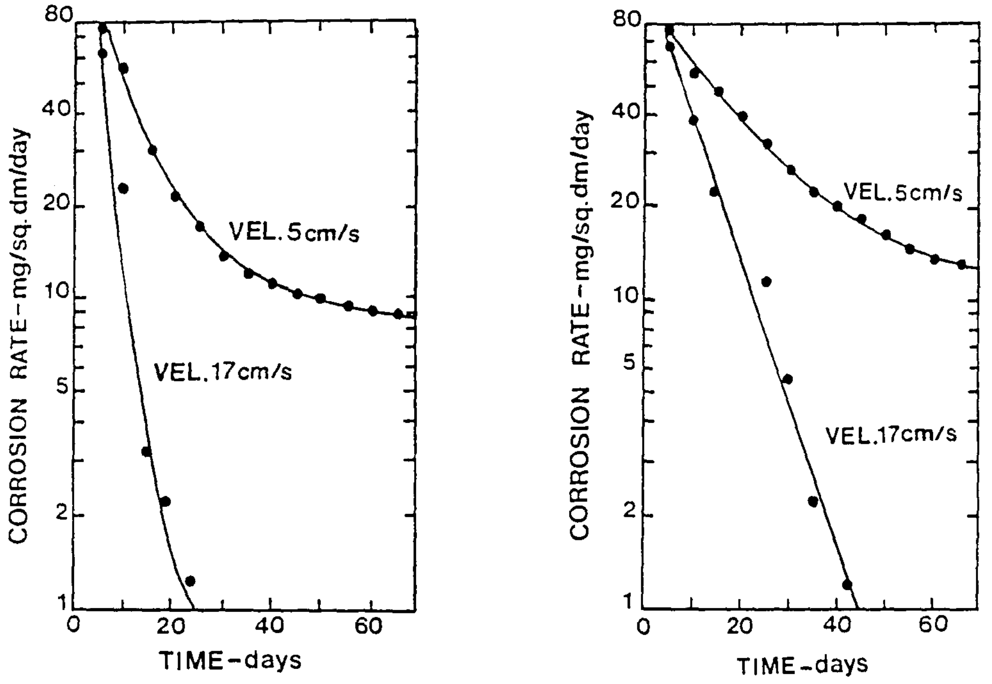
(i) Dissolved oxygen concentration: Dissolved oxygen has a dual influence on the corrosion passivation process. First it acts as an electron acceptor at the cathode thereby increasing the rate of corrosion and the rate of abstraction of protons, H^+, from the water adjacent to the cathode. Second, it may act as an electron acceptor at the anode allowing formation of passivating oxides at this surface. The abstraction of protons at the cathode causes the pH to rise and this in turn causes an increase in the concentration of CO_3^{2-}, and, all things being equal, would tend to increase the rate of $CaCO_3$ precipitation at the surface - the oxygen concentration in the monolayer being the governing criterion. This concentration will depend, inter alia, on the oxygen concentration in the bulk solution and the velocity of flow. No information is available as to the limiting concentration in the bulk solution that will ensure at all times an adequate oxygen supply in the monolayer. Thus it is not possible to lay down substantive rules. For the present one can only recommend that the oxygen concentration should be as high as is practically possible. Probably an oxygen concentration of 4 mg O_2/ℓ would be a reasonable value to aim at.

(ii) Velocity of flow: At low flow velocities the oxygen in the monolayer above the cathode and/or the anode may become limiting, in which event the corrosion rate (and hence the rate of abstraction of protons at the cathode) will slow down. Also, the calcium and carbonate species may become limiting thereby slowing down the $CaCO_3$ precipitation rate at the cathodic surface. At higher velocities it is more unlikely that the calcium, or carbonate or oxygen species will be limiting provided the bulk solution contains sufficient concentrations of these species. Under higher velocity conditions, all things being equal, both the corrosion rate and the $CaCO_3$ precipitation rate are likely to be higher initially; the higher the precipitation rate the more microcrystalline and impermeable will be the $CaCO_3$ precipitant over the cathode, and, the greater the possibility for eventual passivation (via anodic oxide protection, see Section 3.1.1). In contrast, the lower the velocity the more macrocrystalline and permeable the $CaCO_3$ precipitant over the cathode, and, the lower the possibility for passivation.

The effects of high and low velocities on the corrosion rate at pH 7,0 and 8,1 are illustrated in Figs 3.5(a) and 3.5(b) respectively (Miller and Loewenthal, 1982).

Except for pH, both waters had closely the same Alkalinity, calcium, oxygen, chloride and sulphate concentrations. Figure 3.5(a) shows the change of corrosion rate with time at low pH, pH ≈ 7,0, for cast iron in water at two flow velocities, a relatively high flow rate of 17 cm/s, and a low flow rate of 5 cm/s. The chemical condition of the bulk water in both cases was Alkalinity approximately 140 mg/ℓ and calcium approximately 150 mg/ℓ, both as $CaCO_3$, and zero chlorides and sulphates. This water was undersaturated with respect to $CaCO_3$; expressed terms of the Langelier Saturation Index, SI = -0,7; expressed terms of dissolution potential, the water can dissolve approximately 40 mg/ℓ of $CaCO_3$ to reach saturation. For the high flow rate the corrosion rate reduced to almost zero in 30 days, so that one could expect that passivation would be attained; for the low flow rate the corrosion rate reduced from an initial high rate to a virtually constant but still relatively high rate after 70 days, so that it appears doubtful whether passivation can be attained at the low flow rate.

Figure 3.5(b) shows the change of corrosion rates with time at high pH, pH≈ 8,1, for cast iron in water at two flow velocities, a relatively high rate of 17 cm/s, and a low flow rate of 5 cm/s. The water had very nearly the same Alkalinity, calcium, chlorides and sulphates, as that in the example above, except for pH, i.e. Alkalinity = 130 mg/ℓ, calcium = 120 mg/ℓ, both as $CaCO_3$, zero chlorides and sulphates but with pH 8,1. This water was slightly supersaturated with respect to $CaCO_3$; expressed in terms of Langelier Saturation Index, SI = 0,25; in terms of precipitation potential, the water would precipitate 2 mg/ℓ $CaCO_3$ to saturation. Again passivation was attained at the high flow velocity but not at the low flow velocity.



(a) pH = 7,0

(b) pH = 8,1

Fig 3.5(a) and (b) Effect of flow velocity on corrosion rate for cast iron in water with low and high pH, and O_2 = 8 mg O_2/ℓ, temperature 20°C (Miller and Loewenthal, 1982). (a) low pH = 7,0, Alkalinity 144 mg/ℓ, Ca 150 mg/ℓ both as $CaCO_3$. (b) high pH = 8,1, Alkalinity 130 mg/ℓ, Ca 120 mg/ℓ both as $CaCO_3$.

An important conclusion can be drawn from the two examples above: Supersaturation of the bulk solution with respect to calcium carbonate does not in itself guarantee passivation, neither does undersaturation necessarily sustain corrosion. The bulk properties of the water are modified significantly at the boundary by electro-chemical reactions, diffusion and mixing effects, and these may determine whether pacification is attained or not. The experimental data above demonstrates that the water velocity in the pipe can so affect diffusion and mixing that, depending on its magnitude, passivation or continuous corrosion can result.

(iii) Calcium and carbonate species concentrations in the bulk solution: At the cathode, all things being equal, the higher the concentrations of calcium and carbonate species the higher the probability that, with cathodic abstraction of H^+, the state will be supersaturated in the monolayer, microcrystalline calcium carbonate precipitation will take place over the cathode, and a relatively impermeable scale will form.

At the anode, the dissolved carbonate species are thought to have a number of beneficial effects on passivation, Evans (1981). First carbonate and bicarbonate anions reduce the corrosion stimulating effects of chloride and sulphate anions at the anode; this aspect is discussed in detail in (vi) below.

Second, carbonate species that contribute to Alkalinity (HCO_3^- and CO_3^{2-} species) act as a reservoir of OH^- species (formed by hydrolyses of HCO_3^- and CO_3^{2-} species); these OH^- ions are necessary for $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4 and Fe_2O_3 formation at the anode surface. If the total carbonate species concentration, C_T, is high and if the pH of the bulk solution is in the region for high buffering capacity, see (iv) below, a reservoir of OH^- can be maintained at the anode surface without significant pH changes even where the concentration of OH^- is relatively low, i.e. pH $\lesssim$ 8. This is important, for in terms of previous discussion on corrosion termination (Section 3.2), it was postulated that for anodic passivation the rate of tertiary oxide (Fe_3O_4 and Fe_2O_3) formation inter alia should equal or exceed the rate of formation of secondary anodic products ($Fe(OH)_2$ and $Fe(OH)_3$)). Now, the rate of formation of secondary products increases with the OH^- concentration at the anode; at low free OH^- concentrations, pH $\lesssim$ 8, but with high carbonate species concentrations, hydroxide species still are available for secondary products to form, but, this product formation will be relatively slow (because the OH^- concentration is low); thus, the relatively slow rate of secondary product formation allows the tertiary products to form.

Third, a high carbonate species concentration increases the possibility for siderite ($FeCO_3$) precipitation onto the anodic surface. Larson and King (1954), Stumm (1960) and Sontheimer, Kolle and Snoeyink (1981) all speculate that $FeCO_3$ precipitation onto the anode aids passivation, however, they differ in regard to the way that this precipitate effects passivation. Larson suggests that the $FeCO_3$ precipitant seals off cracks that develop with time in protective tertiary anodic ferric oxide films. Stumm (1960) and Sontheimer et al., (1981) suggest that $FeCO_3$ precipitant on the anode in itself does not form a protective scale, but, with time, the $FeCO_3$ precipitate is altered chemically to form a protective anodic film of either calcium carbonate (Stumm) or the iron oxide, Fe_3O_4 (Sontheimer et al.). For the formation of calcium carbonate, Stumm suggests the following reaction

$$FeCO_{3(s)} + Ca^{2+} \rightarrow CaCO_{3(s)} + Fe^{2+}$$

For the formation of Fe_3O_4 (magnetite), Sontheimer et al. suggest

$$3FeCO_{3(s)} + 3H_2O + \tfrac{1}{2}O_2 \rightarrow Fe_3O_{4(s)} + 3H^+ + 3HCO_3^-$$

These reactions are all hypothesized to explain passivation with high calcium and high Alkalinity waters. Support is available from a number of experimental investigations:

Both Larson and Skold (1957) and Miller and Loewenthal (1982) have shown that increase in calcium concentration and Alkalinity leads to a decrease in the average corrosion rate for cast iron. Larson and Skold investigated corrosion of cast iron in waters with calcium concentration varying from 12 to 125 mg/ℓ as $CaCO_3$, Alkalinity 125 mg/ℓ as $CaCO_3$ and with pH values such that all the waters had closely the same saturation index (the authors do not report the value of the saturation index for their experiments, however, assuming that the value was zero, then the respective pH values for the waters with calcium 12 and 125 mg/ℓ as $CaCO_3$ were pH 8,5 and 7,9 respectively). They found that generally the average corrosion rate decreased with increase in calcium concentration.

Miller and Loewenthal (1982) investigated the corrosive behaviour of cast iron in two waters, one with high concentrations of calcium and Alkalinity (315 and 321 mg/ℓ as $CaCO_3$, respectively) and just saturated with respect to calcium carbonate, and the other with relatively low values for calcium concentration and Alkalinity (154 and 156 mg/ℓ as $CaCO_3$, respectively) and undersaturated with respect to calcium carbonate ($CaCO_3$ dissolution potential of 40 mg/ℓ and SI = -0,65); both waters were at the same pH (pH = 7,0) and flow velocity (a relatively low value of 5 cm/s). Figure 3.6 shows observed corrosion rates with time for the two waters. In both waters the corrosion reactions were not completely terminated after 70 days. However, at all times the corrosion rate was significantly lower for the higher calcium/Alkalinity waters. If the velocity of flow had been higher, it is very likely that both these waters would have terminated corrosion. This conclusion is supported by the plots in Fig 3.5b. These plots show the average corrosion rates with time for two waters both with calcium and Alkalinity values close to that of the relatively low calcium/Alkalinity water above but with a high flow velocity of 17cm/s; both waters practically terminated corrosion within 40 days.

(iv) Buffer capacity: According to Stumm (1960) if the pH next to the cathode differs appreciably from that over the anode, the corrosion pattern is one consisting of a relatively small number of large cathodic and anodic regions. If the pH difference is small, the pattern is one of a relatively large number of small cathodic and anodic regions. The latter pattern, Stumm concludes, has a higher likelihood to give rise to passivation. Stumm further comments that the magnitude of the difference in pH between the cathode and anode is affected significantly by the buffer capacity, β, in the bulk solution*. If the buffer capacity is relatively high, the pH difference will be relatively small and vice versa. The buffer capacity in water supplies is determined virtually completely by the total carbonate species concentration (C_T) and the pH. To illustrate this, in Fig 3.7 the buffer capacity with pH is shown for two waters having total carbonate species concentration, C_T, of 100 and 32 mg/ℓ as $CaCO_3$ respectively. In any particular water (with a fixed C_T value) the buffer capacity at pH≈7 is always much greater than at pH≈8. Consequently, in such a water the differences in pH between cathode and anode is always much greater at pH 8 then at pH 7. Or, from the point of view of total carbonate species concentrations, at pH 8 one would need a much greater C_T (i.e. higher Alkalinity and $CO_3^=$ acidity) to give the same pH difference between cathode and anode than for a water at pH 7. Of course, if the C_T for the water is so high that the buffer capacity is appreciable even at pH 8 then, in terms of Stumm's hypothesis, the corrosion pattern is not likely to differ between pH 7 and 8. To test this hypothesis the average corrosion rates with time were measured for cast iron in two waters, one with relatively high buffer capacity of 53,5 mg/ℓ as $CaCO_3$/pH (pH = 7,0, C_T = 177 mg/ℓ, Alkalinity = 144 mg/ℓ and Ca = 150 mg/ℓ all as $CaCO_3$), saturation index -0,7 and calcium carbonate dissolution potential 40 mg/ℓ), and the other with relatively low buffer capacity of 7,2 mg/ℓ as $CaCO_3$/pH (pH 8,1, C_T = 121 mg/ℓ, Alkalinity = 120 mg/ℓ and Ca = 130 mg/ℓ (all as $CaCO_3$), saturation index 0,3 and calcium carbonate precipitation potential 2 mg/ℓ); flow velocity for both 17 cm/s. In Fig 3.8 is shown the average corrosion rates with time of cast iron in each of the two waters. Although the corrosion rate was lower at all times in the higher buffered water, both waters terminated corrosion of cast iron within 40 days (see Fig 3.8). The observed corrosion pattern at pH 7,0 consisted of a relatively large number of small anodic and cathodic sites, whereas at pH 8,1 it consisted of a relatively small number of large anodic and cathodic sites. In so far as the sizes of anodic and cathodic sites are concerned, these observations support Stumm's conclusions. However, bearing in mind that both waters produced nearly complete passivation within 40 days, his conclusion that the nature of the distribution of cathodic and anodic sites also is an important factor in corrosion termination does not necessarily appear to be valid always. Based on Stumm's and Miller and Loewenthal's research, we conclude that buffer capacity or some other pH related parameter gives rise to the differences in distributions of anodic and cathodic regions between pH 7 and pH 8, but, no firm conclusion can as yet be made as to whether such differences influence passivation significantly.

(v) Influence of certain organic material on the nature of $CaCO_3$ precipitate: The effects of trace organics on corrosion rate and passivation have not been comprehensively investigated. However, Larson (1975), Campbell (1971, 1980), Sontheimer et al. (1981)

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*Buffer capacity, β, is defined as the moles/ℓ of strong base, required to effect a unit positive change in pH, i.e. the slope of the strong acid-base titration curve.

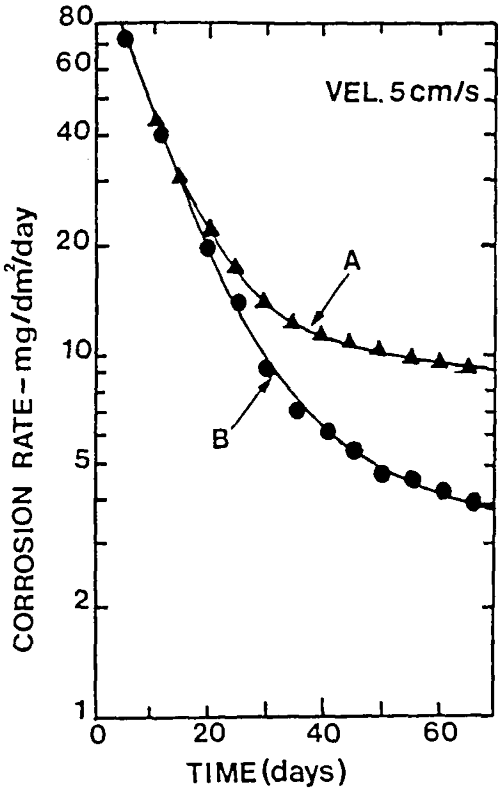

Fig 3.6 Effect of Alkalinity and calcium concentrations on corrosion rate for cast iron in a water with flow velocity 5 cm/sec, oxygen 8 mgO_2/ℓ, pH 7,0 and temperature 20°C. Water A: Alkalinity 119 mg/ℓ, Ca 133 mg/ℓ both as $CaCO_3$. Water B: Alkalinity 321 mg/ℓ, Ca 315 mg/ℓ both as $CaCO_3$

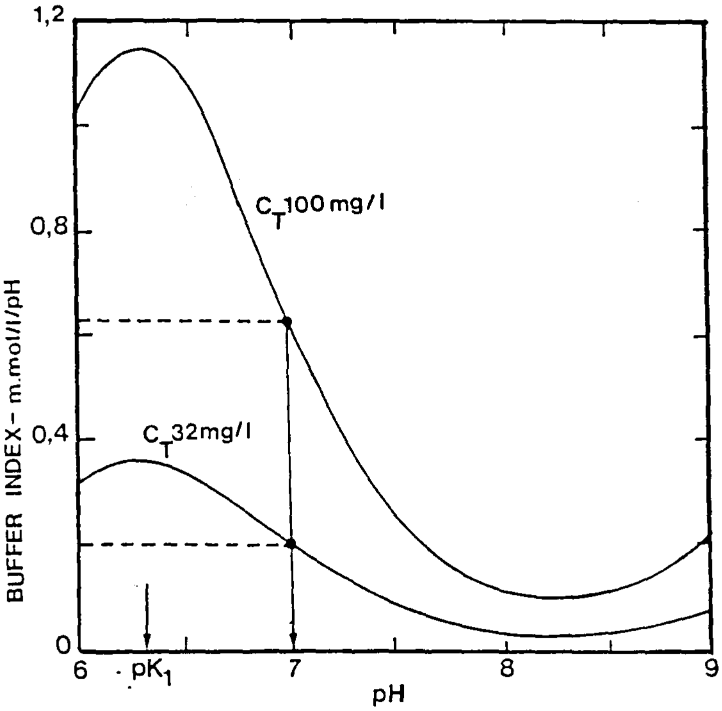

Fig 3.7 Effect of total carbonate species concentration and pH on the buffer capacity of water.

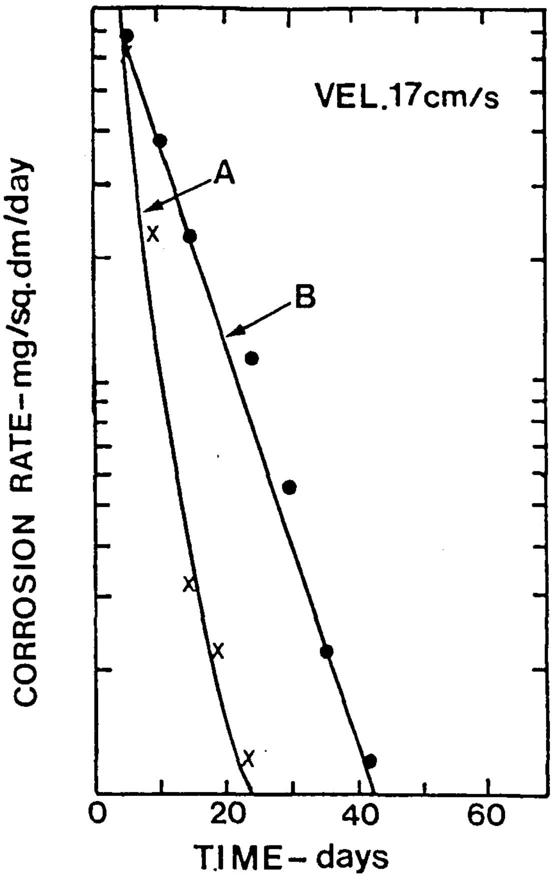

Fig 3.8 Effect of buffer capacity (C_T and pH) on corrosion rate for cast iron in water with flow velocity 17 cm/s and temperature 20°C. Water A: pH 7,0, C_T 177 mg/ℓ, Ca 150 mg/ℓ (both as $CaCO_3$) and buffer 53,5 mg/ℓ as $CaCO_3$/pH. Water B: pH 8,1, C_T 121 mg/ℓ, Ca 130 mg/ℓ (both as $CaCO_3$) and buffer 7,2 mg/ℓ as $CaCO_3$/pH.

and Rudic (1981) have all noted reductions in corrosion rate on addition of natural humic substances to corrosive waters. For example, Larson found a 40 percent decrease in the corrosion rate of Lake Michigan water when spiked with organics from the Illinois River to produce colour equal to 2 platinum-cobalt units.

The nature of the humic substance(s) effecting passivation has not been identified to date and the mechanism is still speculative, but, that it exists is well established. For example, Campbell and Turner (1983) compared the passivating properties of Euston (USA) water, known to contain humic substances, before and after carbon treatment to remove the humics. With humic substances present an eggshell calcium carbonate scale formed on the cathode, without humic substances nodular macro-crystalline calcium carbonate solid deposited. Electrical measurements indicated that both the eggshell and nodular $CaCO_3$ deposits reduced the cathodic area by closely equal amounts, however, the cathode with the eggshell scale polarized more readily than that with the nodular scale. Generally it would appear that polarization of the cathode leads to a decrease in the corrosion current over and above that resulting from the decrease in cathodic area due to $CaCO_3$ precipitation, and, this in turn increases the possibility for final anodic passivation due to oxide formation, as set out in Section 3.1.1.

Summarizing, it appears that the presence of certain humic and other organic substances (as yet unidentified) lead to an eggshell $CaCO_3$ precipite on the cathode which reduces the corrosion current both by decreasing the cathodic area and by polarizing the cathode. Sontheimer et al. suggest that, all things being equal, added corrosion protection is attained when the concentration of humic substances exceeds about 0,6 mg/ℓ (as dissolved organic carbon).

(vi) Chloride and sulphate concentrations: There is general acceptance that chloride and sulphate ions stimulate the rate of corrosion and inhibit passivation. Evans (1981) explains the behaviour as follows: Chloride and sulphate ions are adsorbed onto the anodic surface thereby displacing water and oxygen molecules and hydroxide ionic species; any Fe^{2+} ion released at the anode disperses into the bulk solution where secondary and tertiary reactions can occur giving rise to a finely suspended colloidal form of iron oxides, γFe_2O_3, FeOOH or Fe_3O_4. In consequence no oxide film forms on the anode surface and no passivation is achieved. Furthermore, the presence in solution of sulphate species can give rise to biologically mediated corrosion of iron pipes and fittings. This type of corrosion takes place in micro anaerobic environments, for example within tubercules, both on the inside and outside of iron reticulation pipes. Biologically mediated corrosion is thought to be due to, principally, a bacterial species known as Desulfovibrio desulfuricans which oxidizes solid iron to the ferrous ion (Fe^{2+}) and concommitantly reduces sulphate to sulphide; the ferrous and sulphide ions as well as the hydroxide ions subsequently precipitate as FeS (pyrite), and $Fe(OH)_2$ - none of these form a passivating film, (Kolle and Rosch, 1980). Biologically mediated corrosion appears to be a secondary effect in a corrosive situation - a corrosive situation must exist that causes tubercules to form within which the exacerbating effects of biologically mediated corrosion takes place.

With regard to the corrosion stimulating effects of chlorides and sulphates, the Water Research Centre (1981) in the United Kingdom have suggested that waters containing more than 50 mg/ℓ of either chloride or sulphate should be regarded as potentially corrosive. However as early as 1927 it was observed that the presence in solution of the carbonate species (HCO_3^- and CO_3^{2-}) reduces the corrosive effect of chlorides and sulphates, Evans (1981). According to Evans this ameliorating effect arises from competitive adsorption of the carbonate species onto anodic surfaces, displacing some of the Cl^- and SO_4^{2-} ions. This effect has been investigated further by Larson and his co-workers.

Larson and King (1954) performed corrosion experiments on black plate steel discs (known to be very much less easily corroded than polished cast iron) in aerated water with different pH, Alkalinity, chloride and sulphate concentrations, and very low flow velocity of about 3 cm/s. Their tests were carried out using extremely high Alkalinity waters ($200 < Alk < 800$ mg/ℓ as $CaCO_3$) but with zero calcium. Tests were carried out over a three day period (a very short time for drawing conclusions regarding corrosion). At the end of a three day period they found that the corrosion rate appeared to be linked to the ratio (chloride + sulphate)/Alkalinity; that for Cl^-

/Alkalinity $\lesssim$ 0,2 and SO_4^{2-}/Alkalinity $\lesssim$ 0,25 (with all species concentrations expressed as equivalents) at pH 7,0 the corrosion rate was zero at the end of the test period.

One should note that Larson and King performed their experiments on black steel using a water with zero calcium in solution. This situation deviates from that normally present in municipal water distribution systems where the metal pipe material and fittings would be cast iron and mild steel, and more important, a properly stabilized municipal water invariably should have a calcium concentration of not less than 50 mg/ℓ as $CaCO_3$. Larson and Skold (1958) probably recognized these deficiencies in Larson and King's work and accordingly performed corrosion experiments on polished cast iron specimens in two waters: one with low calcium concentration of 30 mg/ℓ as $CaCO_3$ and just saturated with respect to calcium carbonate (pH 8,2 and Alkalinity 115 mg/ℓ as $CaCO_3$) and a second with relatively high calcium of 85 mg/ℓ as $CaCO_3$ and also just saturated (pH 7,8 and Alkalinity 125 mg/ℓ as $CaCO_3$); for both waters the flow velocity was 25 cm/s. They measured the average corrosion rate over a period of 100 days for ratios of ($C\ell^-$/Alkalinity) from 0,2 to 1,0 (see Fig 3.9). In all the experiments the corrosion

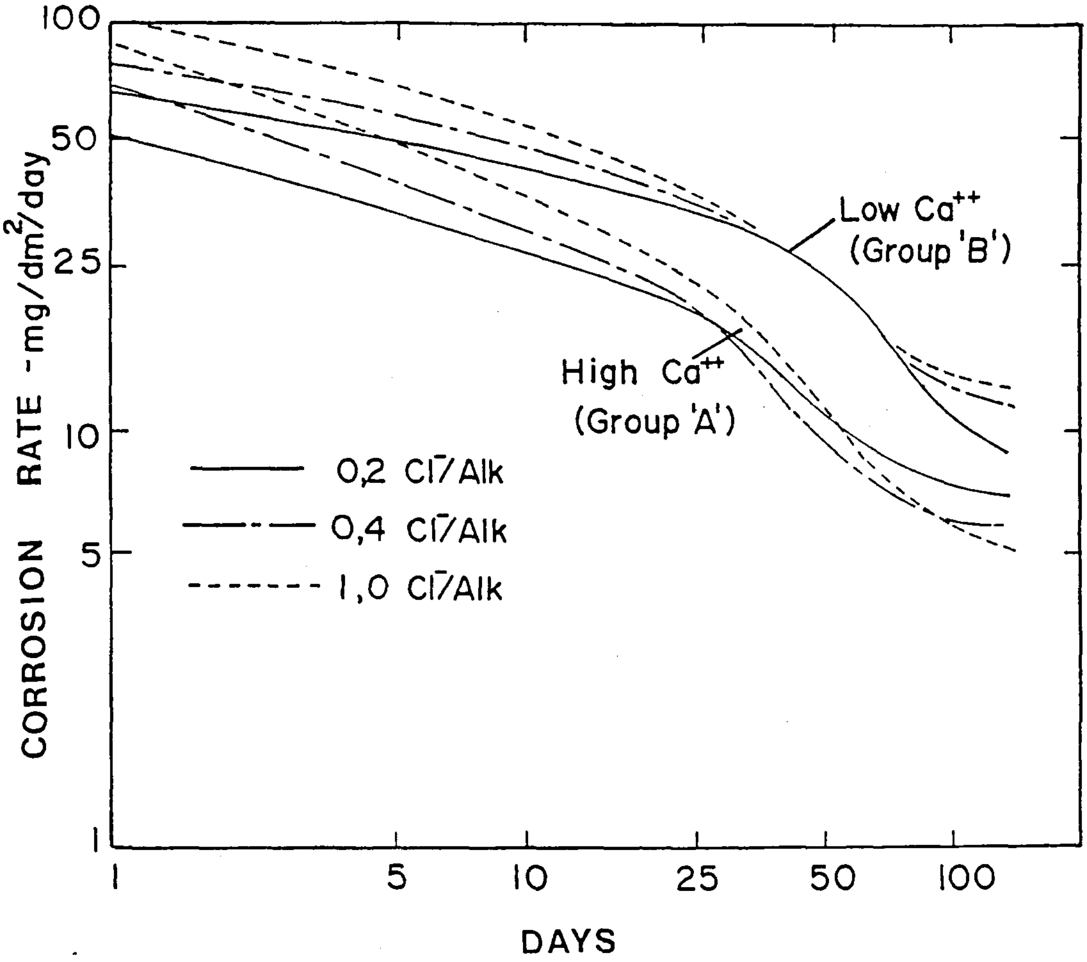

Fig 3.9 Effect of calcium and $C\ell^-$/Alk ratio on corrosion rate for waters saturated with respect to $CaCO_3$ (Flow velocity-m/sec and Alkalinity 125 mg/ℓ as $CaCO_3$). Group A: high Ca of 85 mg/ℓ as $CaCO_3$. Group B: low Ca of 30 mg/ℓ as $CaCO_3$. (After Larson and Skold, 1958).

rate declined with time to about ten percent of the initial rate; furthermore, the corrosion rate always remained higher for the low calcium than the high calcium waters. Whereas corrosion rates initially were higher for higher ratios of ($C\ell^-$/Alkalinity), after about 50 days the corrosion rate appeared to be independent of this ratio. Instead a high calcium concentration produced a clear-cut reduction in corrosion rate. From these results it would seem that calcium content might be an important factor affecting long term passivation in the presence of chloride and sulphate species and might be implicated in the lower limit ratio of ($C\ell^- + SO_4^{2-}$)/Alkalinity for corrosion termination.

Larson (1971) makes the statement that the passivating action of water saturated with respect to calcium carbonate "is decreased by increasing proportions of chloride and sulphate salts above a ratio of 0,1 to 0,2 with respect to alkalinity". This limiting ratio is about the same as that found by Larson and King (1954) for high Alkalinity and zero calcium waters discussed earlier. Larson (1971) neither provides nor quotes supporting data for his statement so that it is not possible to evaluate it critically although the statement is somewhat contradicted by the findings of Larson and Skold (1958).

A number of authors appear to have accepted the upper limiting ratio of ($C\ell^- + SO_4^{2-}$)/Alkalinity $\lesssim$ 0,2 by Larson and King, for example, Merrill and Sanks (1977), Benefield, Judkins and Weand (1982). If it is indeed valid then it would preclude transportion in steel pipes of most of the natural surface water in South Africa. It would seem that all the factors influencing passivation in waters containing sulphates and chlorides have not been sufficiently evaluated; research in this area is merited particularly in the South African context where waters with relatively high sulphate and chloride are common.

Although the effect of corrosion by sulphate and chloride bearing waters cannot be assessed accurately at present, an example where these two species are implicated as agents promoting corrosion has been reported for the City of Johannesburg (Osborn, 1984). Osborn showed that during the period 1940 to 1980 the ratio ($C\ell^- + SO_4^{2-}$)/Alkalinity (all in equivalents) in Johannesburg drinking water increased from about 0,4 to 3,0; during the same period the number of repairs to water mains/unit time followed a similar trend and increased by about eighteen fold (Osborn, 1985). The increase has been in part due to an increase in the size of the reticulation system with population growth and in part has been due to the exacerbating effects of the sulphate reducing organism Desulfovibrio desulfuricans isolated from tuberculed sections, but it would appear that the increase in chlorides and sulphates has intensified the rate of corrosion in the system.

Experimental studies of the potentially corrosive effects of high chlorides and sulphates of typical inland South African waters were undertaken by Miller and Loewenthal (1982). Table 3.1 lists the chemical quality of a synthetic water used in their study and having a chemical constitution of a typical inland water. The results of the corrosion measurements on this synthetic water are plotted in Fig 3.10. The corrosion rate levelled off to a constant high value after about 40 days. It is likely therefore that many inland waters with high chloride and sulphate concentrations may be highly corrosive.

3.4 TENTATIVE GUIDELINES FOR CORROSION PASSIVATION

From the discussion in the previous section one can summarize the conditions under which passivation is likely to occur in water distribution systems: For waters low in chlorides and sulphates, the rate of dissolution of the metal at the anode (Eq 3.1) is a prime factor as to whether a passivating oxide film of γFe_2O_3 or FeOOH or Fe_3O_4 will form or not. For waters high in chlorides and sulphates the formation of a protective film is adversely affected by these ions and requires special consideration. Always the overall corrosion rate is governed by the slower of the two half reactions at the cathode and anode respectively, because the rates of the two half reactions must be equal. Initially the overall reaction rate is high. Interactively this causes changes in the chemical condition of the water layer next to the metal both at the cathode and anode. At the cathode, initially, positively charged colloidal calcium carbonate will form a precipitate cover, if the bulk chemical conditions are appropriate. This precipitate, which is porous to some degree, reduces the rate of ionic and molecular diffusion to the metal surface. While the overall reaction rate still is high, the rate is controlled by the diffusion rate at the cathode. At this stage the film that forms at the anode has no effect on reaction rate because the secondary level reaction products that form are readily permeable and do not isolate the metal. If at the cathode the corrosion reaction is reduced sufficiently by diffusion effects, then at the anode the tertiary reaction(s) can go to completion and form an impervious oxide film on the metal thereby reducing the anodic area so that eventually the overall corrosion rate becomes controlled by the anodic reaction. In time the whole anode is covered by the impervious oxide film giving rise to passivation. Thus, for passivation to occur by film formation, always corrosion needs to precede it. However the presence of chloride and sulphate species will inhibit to some degree the film forming behaviour of the tertiary products at the anode thereby having a deleterious effect on the passivation process.

Table 3.1 Chemical constitution of two waters (a) a typical inland water, Vereeniging treatment works and (b) a synthetic water investigated for corrosivity (see Fig 3.10).

	Alk	Ca^{2+}	SO_4^{2-}	$C\ell^-$	pH	$\frac{C\ell^- + SO_4^{2-}}{Alk}$	SI
	mg/ℓ as $CaCO_3$						
Typical inland water	112	105	250	85	8,1	3,0	+0,1
Synthetic water	142	140	180	170	8,1	2,47	+0,3

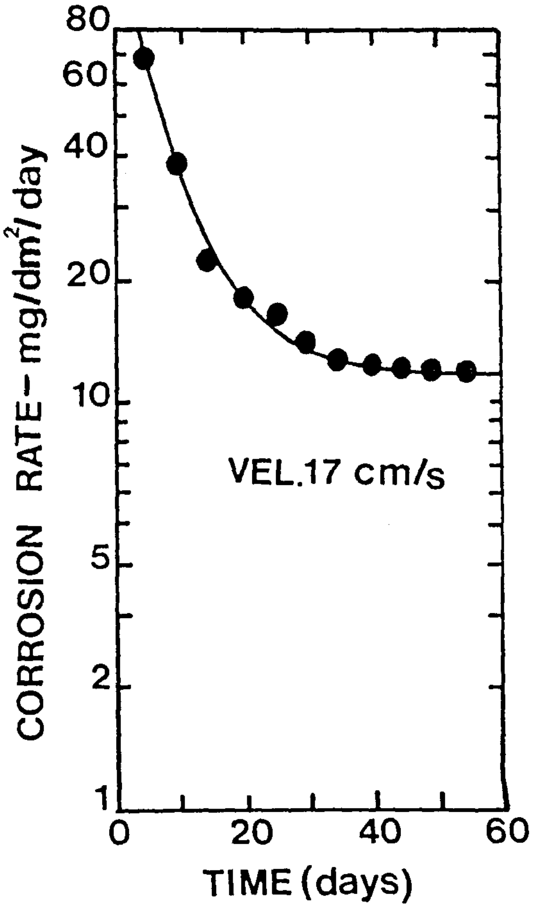

Fig 3.10 Corrosion rate of cast iron with time for a synthetic water (see Table 3.1) with $(C\ell^- + SO_4^{2-})/Alk$ equal to 2,47, Alkalinity 142 mg/ℓ, Ca 140 mg/ℓ (as $CaCO_3$) and pH 8,1. (Test procedure as described by Stumm, 1960).

The factors that influence the corrosion rates and film formation at the anode and cathode are:

(i) Calcium, Alkalinity and pH: Chemical conditions in the water layer at the metal surface may differ appreciably from those in the bulk solution. At the metal surface the pH, carbonate and calcium species concentrations will determine whether colloidal $CaCO_3$ precipitation over the cathode can occur. The state of the water at the surface cannot be estimated from the conditions in the bulk liquid as it depends on the corrosion reaction rate, velocity of flow, buffer capacity and other factors. In consequence no definite limits can be laid down, only guidelines that give a higher likelihood for passivation: it is of importance to note that supersaturation with respect to $CaCO_3$ in the bulk liquid is not essential to obtain passivation - provided supersaturation can be attained at the liquid-solid interface (due to the cathodic corrosion reaction), $CaCO_3$ precipitation still can be attained over the cathode. The degree of undersaturation that can be allowed in the bulk solution however cannot be estimated so that the safest approach should be to maintain, at least, the bulk water at or near saturation with respect to $CaCO_3$. Consequently, the first guideline is:

Guideline 1: The bulk water should be saturated, or slightly supersaturated, with respect to $CaCO_3$. (Where concrete pipes form part of the distribution system the criteria covering non aggression for cement material will automatically satisfy this criterion for metal pipes).

Earlier we stated that observations have indicated that insufficient cathodic protection occurs, via $CaCO_3$ film, if either or both the calcium and Alkalinity concentrations are less than about 50 mg/ℓ (as $CaCO_3$), Larson and Skold (1958). This leads to the second guideline:

Guideline 2: Calcium and Alkalinity values should not be less than 50 mg/ℓ (as $CaCO_3$).

For low Alkalinity-low calcium waters, $CaCO_3$ saturation will entail relatively high pH values, up to pH 9,0; for high Alkalinity - high calcium waters the saturation pH accordingly will be lower. The theory covering the interrelationships between Alkalinity, calcium, pH and saturation is set out in Chapter 4, and applications to problems of conditioning and stabilization and softening of waters is given in Chapter 5.

(ii) Chlorides and sulphates: The presence of chlorides in water tends to sustain corrosion by inhibiting tertiary level anodic film formation, Larson (1955), Larson and Skold (1957, 1958). Sulphates have a similar action, although the indications are that the effect of this species is not as intense as that of chlorides. Bicarbonate and carbonate ions, in contrast, ameliorate the intensity of effects of chlorides (and possibly sulphates). The combined effects of chlorides and bicarbonates and carbonate ions are not yet clearly delineated. Larson concluded that provided the ratio ($C\ell^-$/Alk.) expressed in terms of equivalents is less than 0,2 then the deleterious effects on passivation due to the chlorides will be minimal. The effects of sulphates, although less severe than chlorides, have not been similarly evaluated. Assuming that sulphates have the same effective intensity as chlorides, the requirement becomes: $(C\ell^- + SO_4^{2-})/Alk \leqslant 0,2$.

Guideline 3 (tentative): Two tentative guide lines are suggested:

(1) the ratio $(C\ell^- + SO_4^{2-})$/Alkalinty in equivalents must be less than 0,2 for passivation to be possible.

This guideline has relatively little value in South Africa because so many of the inland waters exceed it. Therefore, the criterion of the Water Research Centre is of greater utility. They suggest that

(2) Waters be regarded as potentially corrosive when either the chloride or sulphate concentration exceeds 50 mg/ℓ.

The present state of knowledge gives virtually no indication as to the rates of corrosion to be expected for waters with quality above the lower limit except that corrosion damage is high when chlorides and sulphates are high. If neither of these guidelines can be satisfied consideration should be given either to substituting metal conduits with conduits of cement type or plastic material, or metal pipes must be lined internally with cement or some other inert coating material.

(iii) Velocity of flow: Even if guidelines (1) to (3) above are satisfied, should the velocity of flow be low in the pipe, corrosion can still continue to occur. The reason for this has been explained in an earlier section as due primarily to oxygen diffusion limitations at the liquid-metal interface. Exactly what the minimum velocity should be cannot be determined unequivocally, but velocities less than about 0,2 m/s are to be avoided and flow velocities of ≥ 1 m/s are to be preferred (Larson and Skold, 1958, McCauley and Abdullah, 1958). The problem of specification of minimum velocities is exacerbated by the daily cyclic flow and velocity pattern in reticulation systems so that no firm recommendation can be made regarding a mean velocity for design purposes. Clearly any design feature that would give rise to dead ends in the system should be avoided. Where low flow velocities are unavoidable in the system, the conduits preferably should be made from cement type or plastic materials. These considerations give rise to the fourth guideline:

Guideline 4: Design conduits in reticulation systems to maintain a velocity in excess of 0,2 m/s (preferably ≥ 1 m/s) and avoid dead ends. Where these conditions are not likely to be satisfied, utilize cement type or plastic pipes; if this is not possible metal pipes (and fittings) must be lined with inert material (for example, paints, tars, cement, plastics or glass fibre).

(iv) Dissolved oxygen concentration: Dissolved oxygen plays a vital role in corrosion and passivation. With low concentrations of dissolved oxygen in the bulk solution it was shown in Section 3.1.2 that a protective film cannot form over the anode and the corrosion continues at some steady rate. At sufficiently high concentrations of dissolved oxygen in the bulk solution, provided guidelines (1) to (4) are satisfied, oxygen is no longer a factor in inhibiting passivation. It is not possible to determine the lower level of oxygen concentration above which corrosion and passivation are independent of oxygen concentration, this will depend on flow velocity, Alkalinity and calcium concentrations and other factors. Usually, if the concentration is greater than about 4 mg/ℓ (as O_2) low oxygen effects will be absent - in general it is advisable to maintain the concentration of oxygen at as high a value as possible. This leads to a fifth guideline:

Guideline 5: The dissolved oxygen concentration in the water should be greater than about 4 mg/ℓ (as O_2).

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Chapter 4

Water Conditioning and the Carbonate System

4.1 INTRODUCTION

In its widest sense the term chemical conditioning of water encompasses addition and removal of chemicals from water to attain a desired quality. Examples of conditioning in water treatment include coagulation, disinfection, stabilization, softening and carbon dioxide stripping. In this monograph only the last three of these processes will be considered.

(a) Stabilization:

Stabilization of water involves conditioning such that it becomes

(i) non aggressive to cement type materials,
(ii) non-corrosive to cast iron and mild steel, and
(iii) not unduly supersaturated with respect to certain minerals (usually $CaCO_3$) so that precipitation on the surfaces of the containing walls will not give rise to such significant accumulation of precipitates that it causes excessive interference with the function of the retaining structure, for example, precipitation on pipe walls giving rise to excessive pipe narrowing and loss in carrying capacity; or in extreme cases, precipitation in the bulk liquid giving turbid waters.

The water quality guidelines to obtain these stability characteristics have been set out in Chapters 2 and 3.

Conditioning of water, to stabilize it, involves adjusting pH, Alkalinity and/or Acidity, calcium concentration and $CaCO_3$ saturation state. Calculations to estimate chemical dosages for stabilization are carried out using equilibrium chemistry in the aqueous phase only. This is done even though it is desired to supersaturate the water with respect to $CaCO_3$. For a slight degree of supersaturation, in the absence of high concentrations of precipitated slurry, the rate of precipitation will be slow so that one may ignore the precipitation reactions and consider only single aqueous phase behaviour. However, precipitation from such waters may take place subsequently in the distribution system with corresponding changes in the chemical constitution of the water. Therefore it is necessary to determine, at the stabilization stage, the expected mass concentration of $CaCO_3$ that can precipitate, and, the aqueous chemical state after precipitation. Such estimations necessarily require analyses involving solid-aqueous phase equilibrium.

(b) Softening:

In water treatment the term softening implies removal from solution of multivalent metallic cation species (i.e. hardness species). These species are removed from waters for general distribution because they interact with soaps and other chemicals to give precipitants that adversely affect washing and many industrial processes. The principal divalent cations in terrestial waters are Mg^{2+}, Ca^{2+}, Fe^{2+} and Mn^{2+}. Of these, Mg^{2+} and Ca^{2+} are likely to be present in most waters; Fe^{2+} and Mn^{2+} usually are found in ground waters devoid of oxygen and in anaerobic bottom waters from stratified eutrophic impoundments. Removal of these species from solution usually is effected through chemical conditioning and precipitation.

The general mechanism by which hardness producing cations are removed from solution is that of precipitation, i.e. by creating conditions whereby the solubility product of a cation with a particular anion is exceeded, whereupon precipitation takes place until the activity product of these ions is again equal to their solubility product. For example, Mg^{2+} is removed by addition of a strong base, i.e. addition of OH^- ions, to exceed the solubility product of $Mg(OH)_2$ to a degree that the concentration of Mg^{2+} will be acceptably low after precipitation. Similarly, Ca^{2+} is removed by increasing the CO_3^{2-} concentration, to exceed the solubility product of $CaCO_3$ by that measure that the concentration of Ca^{2+} will be acceptably low when the activity product of these ions is again equal to their solubility product by precipitation. Fe^{2+} and Mn^{2+} ions are removed by oxidation to the Fe^{3+} and Mn^{3+} and subsequent precipitation of these species as $Fe(OH)_3$ and MnO_2 respectively. This is achieved by aeration (to effect oxidation) and addition of strong base (to effect precipitation). In this monograph only removal of Mg^{2+} and Ca^{2+} will be discussed.

In all the softening dosage calculations it will be assumed that precipitation is complete, i.e. that equilibrium has been established between the aqueous and solid phases. The rate of precipitation is dependent on the measure in which the product of concentrations of the precipitating ions in solution of the precipitating mineral exceed their solubility product, and, the concentration, particle size and crystal structure of solid precipitant. Rapid and complete precipitation is usually assured by having a concentrated slurry of the precipitant in the reactor vessel.

(c) Carbon Dioxide Stripping:

Carbon dioxide (CO_2) exchange between a water body and a gas phase (air) may occur inadvertently, or, may be purposefully induced. The extent to which such exchange takes place depends primarily on the difference in partial pressures of CO_2 between the water and air, the water surface renewal rate, the contact area and contact time between water and air, and mixing conditions in the water body.

In the stabilization of waters with a low level of eutrophication and derived from surface sources (e.g. rivers and impoundments), CO_2 exchange is usually negligible due to the low degree of CO_2 super- or under-saturation and the relatively short time periods the water in the process has contact with the air. In contrast, for surface waters with a high level of eutrophication, there are large diurnal fluctuations in pH (and Acidity) due to photosynthesis (CO_2 abstraction) and respiration (CO_2 injection) by algae and other plants; for such waters large driving forces may be established for CO_2 absorption from the air during the daylight (photosynthetic/respiration periods) and vice versa during the night time (respiration) periods; corresponding to these fluctuations, large masses of CO_2 may be absorbed or expelled by the water body. Yet another situation is that with ground waters; these when brought to the surface may be highly supersaturated relative to the CO_2 partial pressure in the air - the rate of CO_2 expulsion can be very high. The loss of carbon dioxide decreases the Acidity of the water and increases the pH; associated with an increase in pH is an increase in the concentration of CO_3^{2-}. If Ca^{2+} is present, the product $[Ca^{2+}].[CO_3^{2-}]$ may exceed the apparent solubility product for one of the calcium carbonate minerals, and that mineral precipitates. Such waters sometimes contain high concentrations of Fe^{2+} and Mn^{2+} which also precipitate as oxygen is absorbed by the water from the air.

Determination of the mass concentration of CO_2 which can be exchanged between a water body and air involves an analysis of the equilibria between species in the aqueous phase and CO_2 in the gas phase, i.e. aqueous-gas phase equilibrium. Assessment of the concomitant $CaCO_3$ precipitation potential involves an analysis of the equilibrium between species in the aqueous phase, CO_2 in the gas phase and $CaCO_3$ in the solid phase, i.e. aqueous-gas-solid phase equilibrium.

With regard to solving a conditioning problem, for softening or stabilizing a particular water, usually a number of alternative solutions are possible; choice of a particular solution will depend on chemicals available, relative costs of the chemicals and the technical competence available for implementing the conditioning process. To make the optimal choice requires that the alternative chemical dosages be assessed theoretically as expeditiously as possible. Unfortunately the theoretical relationships between variables defining the various equilibrium states are complex. Assessment by numerical analyses is not practical if a computer is not available; however, rapid solutions are possible using graphical plots (called conditioning diagrams) relating the equilibria between the basic system variables (OH^-, H^+, H_2O, $H_2CO_3^*$, HCO_3^-, Ca^{2+}, Mg^{2+} and the associated equilibrium constants) in terms of measureable parameters such as pH and the concentrations of Alkalinity, Acidity and total carbonate species.

In this monograph two types of conditioning charts will be dealt with, (a) Deffeyes type and (b) Modified Caldwell-Lawrence diagrams.

(a) Deffeyes type diagrams: These are single aqueous phase equilibrium diagrams linking pH, Alkalinity, Acidity and total carbonate species (C_T)

(b) Modified Caldwell Lawrence diagrams: These include on one diagram, equilibrium states for (i) single aqueous phase (linking pH, Alkalinity and Acidity), (ii) aqueous-solid phases (linking pH, Alkalinity, Acidity and Ca^{2+} at saturation), (iii) aqueous-gas phases (linking pH, Alkalinity, Acidity and partial pressure of CO_2), and (iv) aqueous-solid-gas phases (linking pH, Alkalinity, Acidity, Ca^{2+} at saturation and the partial pressure of CO_2).

Comparing the two types of diagrams one might conclude that the Modified Caldwell-Lawrence diagram is preferable to the Deffeyes type diagram because the former incorporates all three of the phases whereas the latter deals only with the single aqueous phase. The

Modified Caldwell-Lawrence diagram, however, in order to cover the complete range of parameter values that might be required in conditioning solutions, would need impractically large plots. This situation arises particularly when dealing with low Alkalinity, low calcium, low pH waters, for example, waters derived from the Table Mountain sandstone areas. The difficulty is resolved by using the Deffeyes type diagram to obtain some of the required information, whereupon the solution proceeds on the Modified Caldwell-Lawrence diagram.

To appreciate the procedures involved in chemical conditioning and the application of graphical methods for this purpose, it is necessary to review briefly the equilibrium chemistry of the calcium carbonate system in water. This review is presented using a sequential approach. First, we consider equilibrium between dissolved species, i.e. aqueous phase equilibrium. Here we use weak acid-base stoichiometry both to give a qualitative interpretation of the stoichiometric parameters alkalinity and acidity, and to formulate quantitative expressions for these parameters in terms of weak and strong acid-base species concentrations. Alkalinity and acidity are then linked to pH via weak acid-base equilibrium relationships. These considerations form the basis for the development of the Deffeyes type equilibrium conditioning diagrams. Second, we consider aqueous phase systems that are saturated with respect to solid calcium carbonate. That is, in addition to equilibrium between dissolved species, as in the Deffeyes diagram, we superimpose the requirement of solubility equilibrium between dissolved calcium and carbonate species and solid calcium carbonate, i.e. aqueous-solid phase equilibrium. These considerations form the basis for the development of Modified Caldwell-Lawrence equilibrium conditioning diagrams. Finally, we consider equilibrium between dissolved carbonate species and gaseous carbon dioxide.That is, we consider a system within which equilibrium exists simultaneously both between dissolved carbonate species (i.e. carbonate species in the aqueous phase) and the gaseous carbon dioxide at some partial pressure, i.e. aqueous-gas phase equilibrium. This two phase equilibrium condition is superimposed graphically in the Modified Caldwell-Lawrence diagram. With these additions the diagram can be used for solving problems encompassing aqueous, aqueous-solid, aqueous-gaseous and aqueous-solid-gaseous phases.

4.2 SINGLE AQUEOUS PHASE SYSTEMS

4.2.1 Weak and strong acids and bases

The Arrhenius interpretation of acids and bases will be used, that is, when an acid is added to water it releases hydrogen ions (protons), H^+, and when a base is added it releases hydroxyl ions, OH^-.

Interpreted in terms of an acid or base, water possesses the property of being both at the same time: an extremely small fraction of the water mass dissociates into H^+ and OH^-, giving the following mass balance expression

$$[H_2O] = [H_2O]_{undiss.} + [H_2O]_{diss.}$$
where [ ] = molar concentration.

For pure water (ideality) one can write an equilibrium relationship linking the molar masses of dissociated ions and undissociated water, i.e.

$[H^+][OH^-]/[H_2O]_{undiss.} = K$ (4.1a)

where K = thermodynamic equilibrium constant
= $1,8.10^{-16}$ at 25°C.

The extreme smallness of K implies that $[H_2O]_{diss.}$ is virtually zero compared with $[H_2O]$ i.e. ($[H_2O]$dissociated):($[H_2O]$undissociated) = 10^{-7}:55,5, hence one can substitute in Eq (4.1a)

$[H_2O] = [H_2O]_{undiss.}$

i.e.$[H^+][OH^-]/[H_2O] = K$

This equation is valid for pure water; in pure water the stoichiometric molar concentration (also called "concentration" and designated [ ], is equal to the active molar concentration (also called "activity" and designated ( ), see Chapter 2), i.e.

$(H^+)(OH^-)/(H_2O) = K$ (4.1b)

Transferring (H_2O) to the right hand side and noting that (H_2O) = 55,5 mol/ℓ,

$$\begin{aligned}(H^+)(OH^-) &= (H_2O).K\\ &= 55,5.1,8.10^{-16}\\ &= 10^{-14} = K_w\end{aligned}$$

where K_w is called the thermodynamic ionic product for water.

When an acid, HA, is added to water, two dissociation reactions occur simultaneously, one for the acid and one for the water,

$HA \rightleftarrows H^+ + A^-$
and
$H_2O \rightleftarrows H^+ + OH^-$

and the two equilibrium equations corresponding to these reactions are

$(H^+)(A^-)/(HA) = K_a$ (4.2)
and
$(H^+)(OH^-) = K_w$ (4.1)

where K_a = acid dissociation constant.

When a base, BOH, is added to water, again there are two dissociation reactions with two equilibrium equations, i.e.

$BOH \rightleftarrows B^+ + OH^-$

$H_2O \rightleftarrows H^+ + OH^-$

The corresponding equilibrium equations are

$$(B^+)(OH^-)/(BOH) = K_b \qquad (4.3a)$$

and

$$(H^+)(OH^-) = K_w \qquad (4.1\ )$$

where K_b = base dissociation constant.

Because water dissociates forming both protons and hydroxyl ions and these are related by Eq (4.1), it is possible to interpret a base as an acid and vice versa. That is, the dissociation reaction and equilibrium equation for a base (with its K_b value) can be reformulated as an acid dissociation reaction and equilibrium equation (with a corresponding K_a value). For example, for a base we have the equilibrium dissociation reaction Eq (4.3a),

$(B^+)(OH^-)/(BOH) = K_b$

but from Eq (4. 1)

$(H^+)(OH^-) = K_w$

Substituting for (OH^-) from Eq (4.1) into Eq (4.3a),

$$(BOH)(H^+)/(B^+) = K_w/K_b = K_a \qquad (4.3)$$

The term K_w/K_b is defined as K_a because the form of the left hand side is in terms of (H^+). The advantage of changing the base dissociation to an acid dissociation form, is that the parameter (H^+) is measured in terms of pH (the negative logarithm of (H^+)) irrespective of whether an acid or base is added to water. It is convenient therefore to formulate equilibrium equations in terms of (H^+) rather than (OH^-). Furthermore, by utilizing the acid form of dissociation the pH can serve as a master variable to present both acids and bases in a unified manner, as shall be illustrated below.

Acids and bases are classified as either 'strong' or 'weak' depending on the degree to which these dissociate in water. Strong acids and bases are those that dissociate completely (or very nearly completely) in water; considering the acid form of the dissociation reactions these are identified by having very high and low K_a values respectively - for strong acids $K_a \gtrsim 1$ ($pK_a \lesssim 0$), and for strong bases $K_a \lesssim 10^{-13}$ ($pK_a \gtrsim 13$).

Weak acids and bases are those that dissociate only partially in water; these are identified as having K_a values between those of strong acids and bases, $10^{-13} \lesssim K_a \lesssim 1$ (i.e. $13 \gtrsim pK_a \gtrsim 0$). This division into strong and weak acids and bases can be visually appreciated using a log species-pH plot for each of these systems. In Fig 4.1 are plotted the distribution of species with pH in water for a strong acid (10^{-3} moles/ℓ of HCℓ with pK = -1), a weak acid ($10^{-3,5}$ moles/ℓ of HOCℓ with pK_a = 7,3) and a strong base (10^{-4} moles/ℓ of NaOH with pK_a = 13,5). In this example we assume an ideal solution, i.e. $[Na^+] = (Na^+)$, $[OC\ell^-] = (OC\ell^-)$ etc.

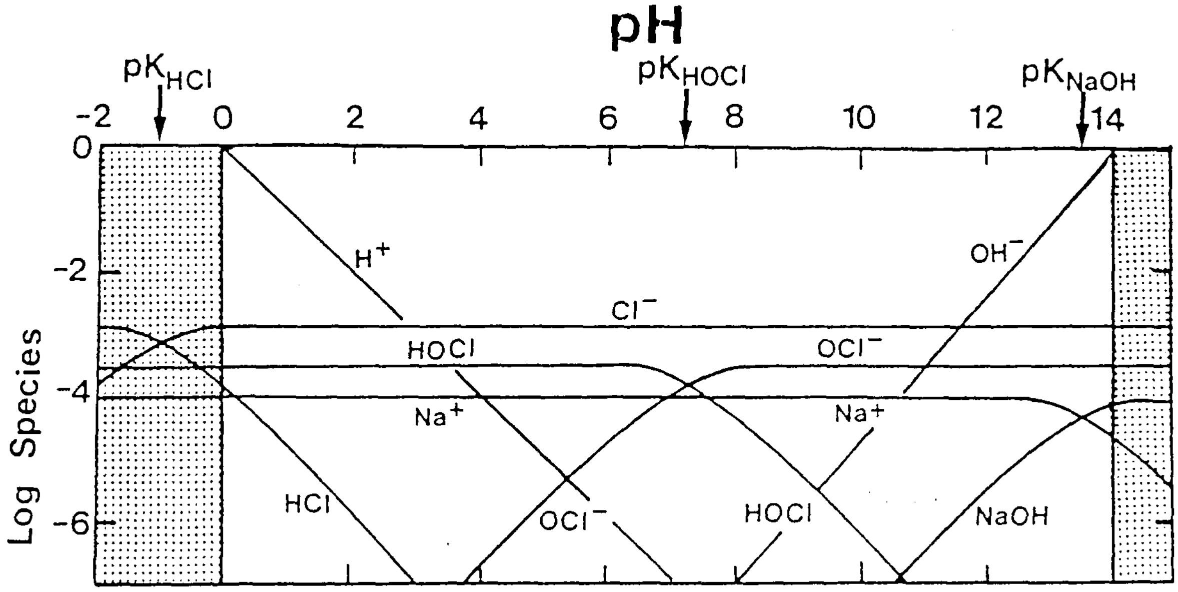

Fig 4.1 Log species-pH plot for a strong acid (10^{-3}molar HCℓ, $pK_a = -1$), a weak acid ($10^{-3,5}$molar HOCℓ, $pK_a = 7,3$) and a strong base (10^{-4}molar NaOH, $pK_a = 13,5$).

These plots are obtained by noting that, for the acid HAc, the total acid species, A_T, after dissociation is made up of HAc and Ac^-, i.e.

$$A_T = [HAc] + [Ac^-]$$

With this equation together with the two equilibrium equations

$$(Ac^-)(H^+)/(HAc) = K_a$$

and

$$(H^+)(OH^-) = K_w,$$

for a fixed A_T value, one can solve for (HAc), (Ac^-), (H^+) and (OH^-) in terms of $-\log_{10}(H^+)$, i.e. pH. One can deal with the base, BOH, in a similar fashion using the acid form of dissociation.

From Fig 4.1, strong acids and bases are virtually completely dissociated in the pH range $12 \gtrsim pH \gtrsim 2$. In contrast, weak acids, for example the HOCℓ system, have relative concentrations of HOCℓ and dissociated species, $OC\ell^-$, that vary significantly in the pH range of normal waters; in the region pH < pK_a the weak acid species are principally in undissociated form, (HOCℓ), and, in the region pH > pK_a principally in the dissociated form $(OC\ell^-)$. Similarly, for weak bases, the base species are principally in the undissociated form BOH in the region pH > pK_a, and in the dissociated form, B^+, in the region pH < pK_a.

A weak acid species that releases only a single proton is termed a monoprotic weak acid. However there are weak acids which can release more than one proton on dissociation, for example phosphoric acid, H_3PO_4, can release up to three protons and is termed a triprotic weak acid. In natural waters the dominating weak acid system is the diprotic carbonate system, existing in solution as $H_2CO_3^*$, HCO_3^- and CO_3^{2-}. For this system we identify two acid dissociation reactions[†]:

(i) dissociation of $H_2CO_3^*$ to HCO_3^- and H^+, with a corresponding pK_a value of $pK_1 = 6{,}33$ at T = 25°C, (Harned and Davies, 1943) i.e.

$$H_2CO_3^* \rightleftarrows HCO_3^- + H^+$$

and (ii) dissociation of HCO_3^- to CO_3^{2-} and H^+, with a corresponding $pK_2 = 10{,}40$ at T = 25°C, (Harned and Scholes, 1943) i.e.

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+.$$

In terms of our definition of strong and weak acid reactions, each of the two reactions above correspond to weak acid-base reactions. The distribution of carbonate species with pH, at infinite dilution, is shown in Fig 4.2. Referring to this plot, in the region $pH < 6{,}3$ the $H_2CO_3^*$ species dominates, in the region $6{,}3 < pH < 10{,}4$ the HCO_3^- species dominates, and in the region $pH > 10{,}4$ the CO_3^{2-} species dominates.

4.2.2 Carbonate species equilibria

Carbonate species dissolved in water exist as molecularly dissolved carbon dioxide, CO_2aq, and carbonic acid H_2CO_3; and the ionic species, bicarbonate, HCO_3^-, and carbonate CO_3^{2-}. The dissolved species exist in equilibrium with each other and with the water molecules, hydroxide ions OH^- and hydrogen ions H^+. The following thermodynamic equilibrium equations must be satisfied simultaneously:

(i) Dissociation of water

$$(H^+)\,(OH^-) = K_w \tag{4.4}$$

(ii) Dissociation of carbonic acid

$$\frac{(H^+)\,(HCO_3^-)}{(H_2CO_3^*)} = K_1 \tag{4.5}$$

where $(H_2CO_3^*) = (H_2CO_3) + (CO_2aq)$

(iii) Dissociation of the bicarbonate ion

$$\frac{(H^+)\,(CO_3^{2-})}{(HCO_3^-)} = K_2 \tag{4.6}$$

[†] The species $H_2CO_3^*$ refers to the sum of carbonic acid, H_2CO_3, and molecularly dissolved carbon dioxide, $CO_{2(aq)}$, see Stumm and Morgan, 1970.

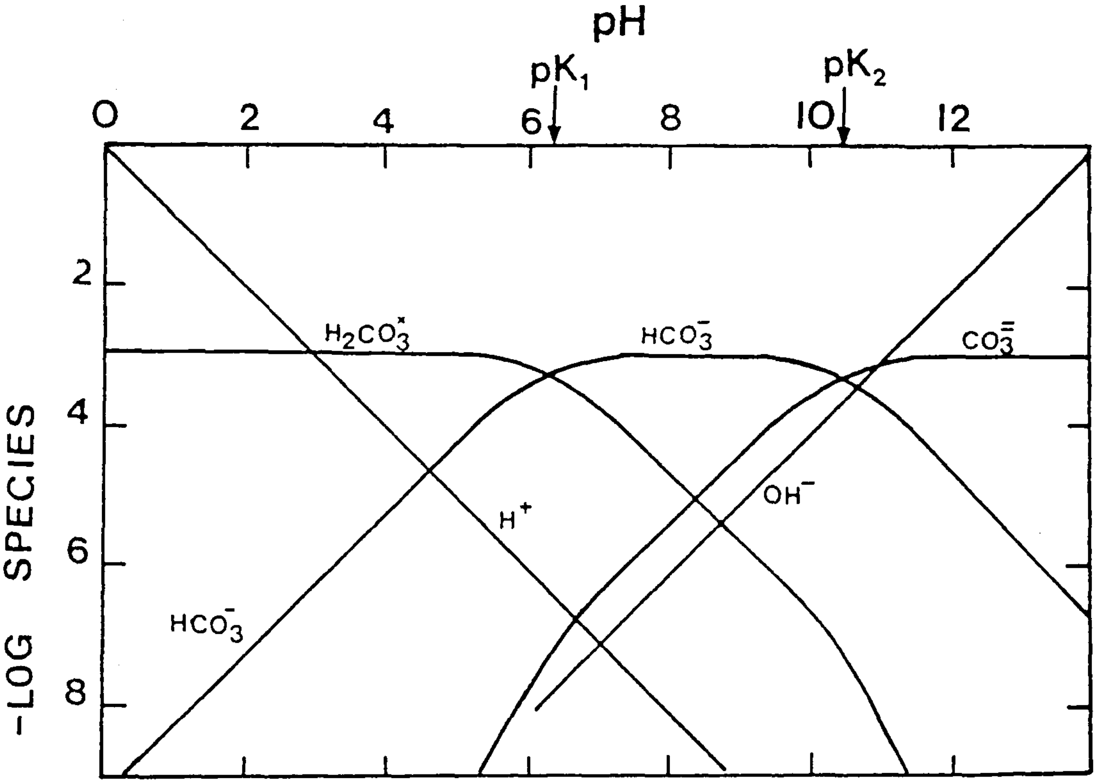

Fig 4.2 Log species-pH plot for the carbonate system in water with C_T = 10^{-3}M (pK_1 = 6,33 and pK_2 = 10,40 at 25°C and infinite dilution).

where ( ) = activity* of species in solution.

The thermodynamic equilibrium and ionic product constants K_1, K_2 and K_w in Eqs (4.4 to 4.6) vary with temperature as follows:

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

$$pK_w = 4787{,}3/T + 7{,}1321 \log T + 0{,}01037\ T - 22{,}801$$

(ii) For pK_1 from Harned and Davis (1943)

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

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

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

where $pX = -\log_{10}(X)$
T = temperature in Kelvin

---

*For definition of the term activity, etc. see Section 2.1, Chapter 2

The thermodynamic equilibrium equations, Eqs (4.4 to 4.6), we have seen, are expressed in terms of activities. In practice however only one parameter in these equations, (H^+), can be measured directly in terms of activity via pH, i.e.

$$pH = -\log(H^+) \tag{4.7}$$

All the other parameters in Eqs (4.4 to 4.6) eventually are determined in the concentration form as they are derived from mass parameters (e.g. Alkalinity, Acidity and total carbonate species concentration) which are determined in stoichiometric (concentration) form (see Section 2.1 Chapter 2). Therefore Eqs (4.4 to 4.6) need to be transformed with all the species, in the concentration form, except for H^+.

Transformation of the equilibrium equations from the activity to the concentration form, is via the link between activity and concentration, (see Section 2.1 Chapter 2), i.e. activity equals the product of concentration and an activity coefficient. Rewriting the equilibrium equations Eqs (4.4 to 4.6) with weak acid species activities formulated as the product of concentration and activity coefficients, we have:

$$(H^+)\, f_{OH^-} . [OH^-] = K_w \tag{4.4a}$$

$$\frac{(H^+)\, f_{HCO_3^-}\, [HCO_3^-]}{[H_2CO_3^*]} = K_1 \tag{4.5a}$$

$$\frac{(H^+)\, f_{CO_3^{2-}}\, [CO_3^{2-}]}{f_{HCO_3^-}\, [HCO_3^-]} = K_2 \tag{4.6a}$$

where $f_{HCO_3^-}$, $f_{CO_3^{2-}}$, f_{OH^-} = activity coefficients for HCO_3^-, CO_3^{2-} and OH^- respectively. For the uncharged species $H_2CO_3^*$ the activity coefficient very closely approximates unity in low salinity waters, so that $[H_2CO_3^*] = (H_2CO_3^*)$.

Lumping the activity coefficients of the weak acid species with the equilibrium constants, one obtains equilibrium equations in a practical useful form for analysis: Transferring the activity coefficients to the right hand side of Eqs (4.4a to 4.6a),

$$(H^+)\,[OH^-] = \frac{K_w}{f_{OH^-}} = K'_w \tag{4.8}$$

$$\frac{(H^+)\,[HCO_3^-]}{[H_2CO_3^*]} = \frac{K_1}{f_{HCO_3^-}} = K'_1 \tag{4.9}$$

$$\frac{(H^+)\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_2\, f_{HCO_3^-}}{f_{CO_3^{2-}}} = K'_2 \tag{4.10}$$

where K'_w, K'_1 and K'_2 now are termed apparent equilibrium constants.

The activity coefficients used in Eqs (4.8 to 4.10), to calculate K_w', K_1' and K_2', are readily estimated for low salinity waters using the Debye-Hückel equation (valid for ionic strength $<$ 0,01, TDS $<$ 400 mg/ℓ) or a variation of this equation, such as the Davies equation (valid for ionic strength $<$ 0,1, TDS $<$ 4000 mg/ℓ) as set out in Eq (2.5) Chapter 2. Thus, in the three equilibrium equations Eqs (4.8 to 4.10), if the temperature and ionic strength are known, the apparent constants K_w', K_1' and K_2' can be determined.

The equilibrium equations, Eqs (4.8 to 4.10), incorporate five unknowns, (H^+), $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ and $[OH^-]$. As there are only three independent equations linking these five unknowns, at least two parameters must be measured to define the state of the system. For low salinity waters, if a pH meter is properly standardized the activity of H^+, i.e. (H^+), is found directly from the pH reading via Eq (4.7). The remaining unknown is found by deriving parameters which can be measured and are functions of the basic parameters H^+, OH^-, CO_3^{2-}, HCO_3^- and $H_2CO_3^*$. A number of such functions have been developed giving rise to the concepts of alkalinity, acidity and total carbonate species concentration. It is necessary therefore to review briefly how these parameters are developed, what they imply and how they can be measured.

4.2.3 Alkalinity, acidity and total carbonate species concentration

Alkalinity and acidity: In order to understand the meaning of alkalinity and acidity it is necessary to establish some key aspects relating to weak-base systems:

(i) If a weak acid or base, or the salt of a weak acid or base, is added to pure water the solution is called an equivalent solution and the pH established is called the equivalence point for the weak acid or base, or salt of the weak acid or base.

(ii) If a strong base (e.g. NaOH) is now added to one of the equivalent solutions above, the pH will increase above the equivalence point and the mass concentration of base added is called the alkalinity with respect to a designated equivalent solution. This alkalinity can be measured by back titrating the solution with standard strong acid to an endpoint pH at the equivalence point, the mass of standard acid added then being equal to the base added, i.e. equal to the alkalinity of the water. If a strong acid is added to an equivalent solution, the pH will drop below the equivalence point and the acid added is called the acidity with respect to the equivalent solution. Similar to the alkalinity measurement, acidity can be determined by back titrating the solution with a standard strong base to the endpoint pH at the equivalence point. Thus, the equivalence point of a weak acid and/or base is the reference point when titrating to measure the associated alkalinity or acidity in the solution.

In natural terrestial waters the dominating weak acid-base system is the carbonate system existing as $H_2CO_3^*$, HCO_3^- and CO_3^{2-} species in solution. If carbon dioxide is added to pure water we have an equivalent carbonic acid ($H_2CO_3^*$) solution; if HCO_3^- is added as a bicarbonate salt we have an equivalent HCO_3^- solution; and if CO_3^{2-} is added as a carbonate salt an equivalent CO_3^{2-} solution; each respectively gives rise to its associated equivalence point (see Fig 4.2). To these respective equivalent solutions one can add a base (alkalinity) or acid (acidity); back titration to the respective equivalence points will give the alkalinity or acidity that had been added to the respective equivalent solutions. Thus, one may have $H_2CO_3^*$ alkalinity or $H_2CO_3^*$ acidity relative to the $H_2CO_3^*$ equivalence point depending on whether the initial pH is above or below the $H_2CO_3^*$ equivalence point; HCO_3^- alkalinity or HCO_3^- acidity relative to the HCO_3^- equivalence point, and CO_3^{2-} alkalinity or CO_3^{2-} acidity relative to the CO_3^{2-} equivalence point.

Theoretically, if the carbonate system in solution is characterized (by knowing values of any two independent parameters from C_T, pH and one or more of the various alkalinities and acidities) then the equivalence points are defined. Practically, however, no information is available on a solution initially except for pH. To measure any alkalinity or acidity the corresponding equivalence point needs to be identified; in this regard there are the following difficulties:

(1) An equivalence point may change with the magnitude of the mass concentration of carbonate species in the solution, C_T. So, for example, equivalent $H_2CO_3^*$ solutions, of 10^{-3} mol/ℓ and 10^{-4} mol/ℓ, will have equivalence points at pH = 4,6 and pH = 5,15 respectively; similarly equivalent CO_3^{2-} solutions have equivalence points that vary with C_T. In contrast, the HCO_3^- equivalent solution has an equivalence point that is virtually independent of the total carbonate species concentration. This is illustrated in Fig 4.3 in which the distribution of the logarithms of species concentrations is plotted versus pH for two waters - one with $C_T = 10^{-3}$ mol/ℓ and the other with $C_T = 10^{-4}$ mol/ℓ. The $H_2CO_3^*$ equivalence point lies at the intersection of lines representing H^+ and HCO_3^- species, i.e. at Points 1 and 1' for the high and low C_T waters with pH values pH = 4,6 and 5,15 respectively; the HCO_3^- equivalence points at the intersection of lines representing $H_2CO_3^*$ and CO_3^{2-} species, i.e. at Points 2 and 2' for the high and low C_T waters - both at the same pH, pH = 8,4; and the CO_3^{2-} equivalence points at the intersection of lines representing HCO_3^- and OH^- species, i.e. at Points 3 and 3' for the high and low C_T waters with pH values pH = 10,6 and 9,8 respectively.

(2) The equivalence point might lie in a pH region where a large mass of acid or base gives rise to a small change in pH, that is, the back titration endpoint is in a region of high buffer capacity. In such an event, even if one knows the endpoint pH, the back titration can be substantially in error for a small error in the titrated endpoint. This situation applies to the CO_3^{2-} equivalence point, which in consequence, makes that its associated alkalinity or acidity determination is not practical. In contrast, the $H_2CO_3^*$ and HCO_3^- equivalence points lie in pH regions of low buffer capacity; these two endpoints in this regard, therefore are to be preferred to the CO_3^{2-} endpoint.

The discussion above indicates that the alkalinity or acidity determination to the HCO_3^- equivalence point should be the most appropriate one because the equivalence point is independent of the total carbonate species concentration <u>and</u> lies in a pH region of low buffering capacity. However, in titrating to an endpoint we wish to obtain information not only on alkalinity and/or acidity, but also on the total carbonate species C_T. If one has the pH of the water and any one of the alkalinity or acidity measurements then theoretically one should be able to define the carbonate system completely. However, if the pH of a sample is at the HCO_3^- equivalence point, then the zero value for alkalinity/acidity to this equivalence point gives no information regarding the carbonate species because the pH at this equivalence point is independent of C_T (see Fig 4.3), consequently, C_T can have any value for the same pH. Furthermore,if the pH is near this equivalence point, then, being in a region of low buffer capacity, only a small mass of titrant will be needed to the endpoint. This gives rise to an unreliable alkalinity or acidity determination. This is a situation often encountered with terrestial waters (i.e. pH in the range 7,8 to 8,5). For these reasons the most useful and practical measurement parameters to quantify the carbonate system, are the pH of the water and the $H_2CO_3^*$ alkalinity i.e. the alkalimetric titration to the $H_2CO_3^*$ equivalence point.

Theoretically one can derive equations linking the alkalinities and acidities to the carbonate species ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) and the water species ($[H^+]$ and $[OH^-]$). We shall state these only, for the derivations refer to Loewenthal and Marais (1976). These alkalinities and acidities are mass parameters because they reflect the mass concentrations of acid or base to be added to bring the pH to the specified equivalence point.

To the $H_2CO_3^*$ equivalence point:

If initial pH is greater than this equivalence point,

$$H_2CO_3^* \text{ alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \qquad (4.11)$$

and, if less

$$H_2CO_3^* \text{ acidity} = [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] \qquad (4.12)$$

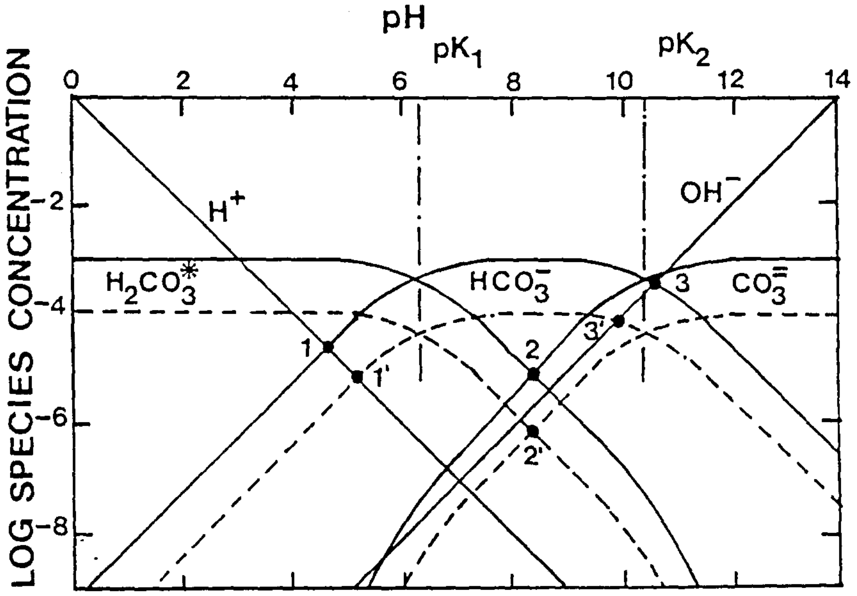

Fig 4.3 Log species-pH diagrams for two waters with $C_T = 10^{-3}$ and 10^{-4} mol/ℓ. $H_2CO_3^*$ equivalence point occurs at pH Points 1 and 1' and varies with C_T. HCO_3^- equivalence point occurs at pH of Points 2 and 2' and is independent of C_T.

To the HCO_3^- equivalence point:

If initial pH is greater than this equivalence point,

$$HCO_3^- \text{ alkalinity} = [CO_3^{2-}] + [OH^-] - [H_2CO_3^*] - [H^+] \qquad (4.13)$$

and, if less

$$HCO_3^- \text{ acidity} = [H_2CO_3^*] + [H^+] - [CO_3^{2-}] - [OH^-] \qquad (4.14)$$

To the CO_3^{2-} equivalence point:

If initial pH is greater than this equivalence point,

$$CO_3^{2-} \text{ alkalinity} = [OH^-] - [H^+] - [HCO_3^-] - 2[H_2CO_3^*] \qquad (4.15)$$

and, if less

$$CO_3^{2-} \text{ acidity} = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-] \qquad (4.16)$$

Historically the alkalinities and acidities associated with the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points have been assigned special names which have somewhat obscured their basic meanings. The theoretical and historical nomenclatures are compared in Table 4.1.

The consistent nomenclature described above can be applied to all weak acid-base systems e.g. phosphate, ammonia, acetate etc. systems. The generality of the approach commends its use. For this reason we will employ the consistent approach extensively in this monograph. However, because $H_2CO_3^*$ alkalinity and CO_3^{2-} acidity are the dominant alkalinity and acidity parameters used in analyses of the carbonate system, we will make one concession for convenience and use interchangeably Alkalinity for $H_2CO_3^*$ alkalinity and Acidity for CO_3^{2-} acidity. Consequently, wherever the terms Alkalinity and Acidity are used these imply $H_2CO_3^*$ alkalinity and CO_3^{2-} acidity respectively, and vice versa.

The equations for the alkalinities and acidities in the nomenclature in use today, to each of the three equivalence points are:

(i) Total alkalinity, or Alkalinity or methyl red alkalinity ($H_2CO_3^*$ alkalinity):

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

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

(ii) Phenolpthalein alkalinity (HCO_3^- alkalinity):

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

Table 4.1 Theoretical and historical nomenclature for alkalinities and acidities associated with the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points.

Theoretical nomenclature	Historical nomenclature
$H_2CO_3^*$ alkalinity	Total alkalinity, methyl red alkalinity or Alkalinity.
$H_2CO_3^*$ acidity	Mineral acidity
HCO_3^- alkalinity	Phenolpthalein alkalinity
HCO_3^- acidity	CO_2 acidity
CO_3^{2-} alkalinity	Caustic alkalinity
CO_3^{2-} acidity	Total acidity or Acidity.

$$\text{Phenolphthalein alkalinity} = [CO_3^{2-}] + [OH^-] - [H_2CO_3^*] - [H^+]$$

(iii) Caustic alkalinity (CO_3^{2-} alkalinity):

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

$$\text{Caustic alkalinity} = [OH^-] - 2[H_2CO_3^*] - [HCO_3^-] - [H^+]$$

(iv) Total acidity, or Acidity (CO_3^{2-} acidity):
An equivalent solution of CO_3^{2-} plus a net strong acid,

$$\text{Acidity} = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-]$$

(v) CO_2 acidity (HCO_3^- acidity):

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

$$CO_2 \text{ acidity} = [H_2CO_3^*] + [H^+] - [CO_3^{2-}] - [OH^-]$$

(vi) Mineral acidity ($H_2CO_3^*$ acidity):

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

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

Total carbonate species concentration:

An additional mass equation is that for the total carbonate species concentration in the solution. The total carbonate species concentration, C_T, is defined as the sum of concentrations in solution of the individual carbonate species $H_2CO_3^*$, HCO_3^- and CO_3^{2-}, i.e.

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{4.17}$$

4.2.4 Interdependence between mass parameters

Referring to the mass equations, Eqs (4.11 to 4.17), each equation adds a new variable to the system so that irrespective of the number of additional equations, the number of independent unknowns remains equal to two. Consequently, if values are known for any two of these parameters then the remaining ones can be determined, or alternatively, if values for pH and one mass parameter are known the system can be solved (see Section 4.2.5). It also follows that the mass concentrations of C_T and the various forms of alkalinity and acidity are not independent. Two forms of interdependence exist: (a) between alkalinity and acidity relative to a particular equivalence point, and (b) between alkalinities and acidities relative to different equivalence points.

(a) For the alkalinity and acidity associated with a particular equivalence point, the alkalinity value is simply the negative of the acidity value, i.e.

(i) For the $H_2CO_3^*$ equivalence point, from Eqs (4.11 and 4.12)

$$H_2CO_3^* \text{ alkalinity (Alkalinity)} = -\text{ve } H_2CO_3^* \text{ acidity} \tag{4.18}$$

(ii) For the HCO_3^- equivalence point, from Eqs (4.13 and 4.14),

$$HCO_3^- \text{ alkalinity} = -\text{ve } HCO_3^- \text{ acidity} \tag{4.19}$$

(iii) For the CO_3^{2-} equivalence point, from Eqs (4.15 and 4.16),

$$CO_3^{2-} \text{ acidity (Acidity)} = -\text{ve } CO_3^{2-} \text{ alkalinity} \tag{4.20}$$

(b) Interdependence between alkalinities and acidities for different equivalence points:

(i) Adding Eqs (4.11 and 4.16),

$$\text{Alkalinity} + \text{Acidity} = 2\,C_T \tag{4.21}$$

(ii) Subtracting Eq (4.16) from Eq (4.11),

$$\text{Alkalinity} - \text{Acidity} = 2\,HCO_3^- \text{ alkalinity} \tag{4.22}$$

(iii) Adding Eqs (4.16 and 4.13)

$$\text{Acidity} + HCO_3^- \text{ alkalinity} = C_T \tag{4.23}$$

(iv) Subtracting Eq (4.11) from Eq (4.16)

$$\text{Acidity} - \text{Alkalinity} = 2.HCO_3^- \text{ acidity} \qquad (4.24)$$

Equations for the mass parameters, Eqs (4.11 to 4.17), and their interdependence, Eqs (4.19 to 4.24), are represented graphically in Fig 4.4 with Alkalinity and Acidity as co-ordinate parameters. Clearly Fig 4.4 reflects the fact that if values are known for two independent mass parameters then values for the remaining parameters can be determined directly.

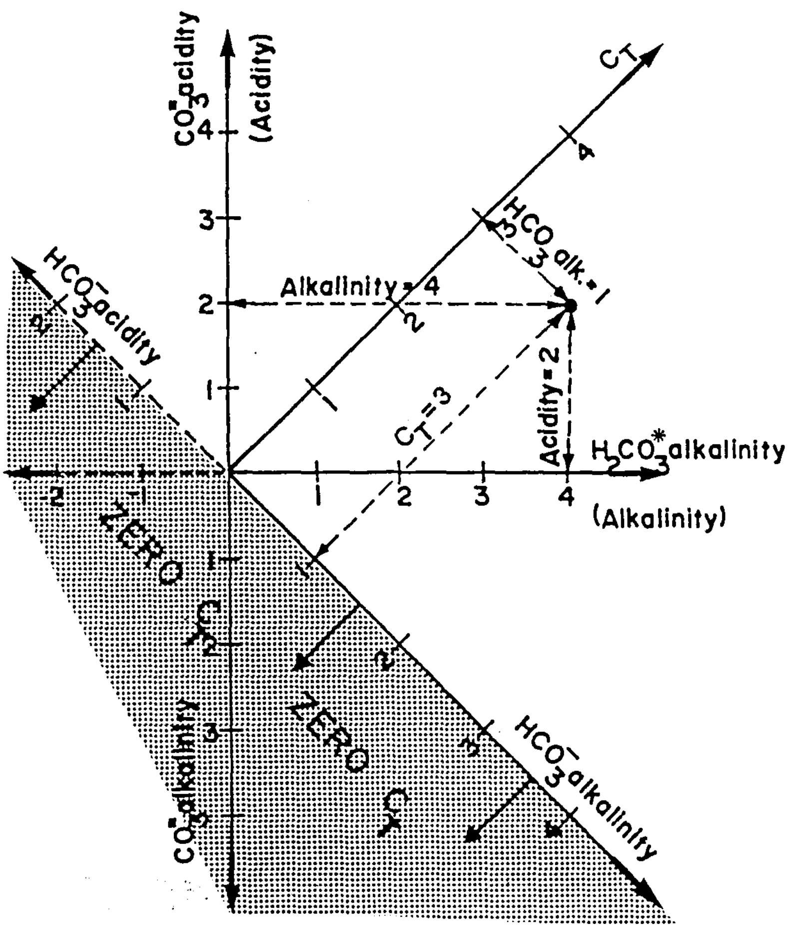

Fig 4.4 Interdependence between mass parameters for the carbonate system.

4.2.5 Interdependence between pH and mass parameters

As set out in Section 4.2.4 above, measurement of two independent mass parameters for the carbonate system directly allows values for the remaining mass parameters to be calculated. Historically, Alkalinity and Phenolpthalein Alkalinity (HCO_3^- alkalinity) were the two parameters measured, usually by titration to the respective colorimetric endpoints (with their associated uncertainty). However, with the availability of pH meters a widely used practice has developed to measure one mass parameter, Alkalinity (via pH-potentiometric methods), and obtain the other independent parameter by measuring pH of the raw water. Consequently, a major advantage is to be gained if the pH can be superimposed on the mass parameter diagram, because, having pH and Alkalinity measurements, the carbonate system then will be defined completely in terms of any two mass parameters, and hence in terms of carbonate species via Eqs (4.11 to 4.17).

The interdependence between pH, Alkalinity and Acidity is established via the equilibrium equations, Eqs (4.8 to 4.10) and the mass equations for Alkalinity and Acidity, Eqs (4.11 and 4.16) (Loewenthal and Marais, 1976), to give

$$\text{Alkalinity} = \left[\frac{1 + 2.10^{(pH-pK_2')}}{1 + 2.10^{(pK_1'-pH)}}\right] \cdot \left[\text{Acidity} + 10^{(pH-pK_w')} - 10^{-pH}\right] \qquad (4.25)$$

where Alkalinity and Acidity are in mol/ℓ.

Examination of Eq (4.25) shows that for a fixed value of pH there is a linear relationship between Alkalinity and Acidity. That is, for a selected pH value, with Alkalinity and Acidity as co-ordinate axes, the selected pH will plot as a straight line. Figure 4.5 shows a family of pH lines plotted with Alkalinity and Acidity as co-ordinate axes. This plot is for ionic strength 0,001 and temperature 15°C. (The ionic strength and temperature dependence for the plot arises from the pK' values in Eq 4.25). Figures 4.4 and 4.5 can be superimposed (see Fig 4.5) to give a general graphical description of interdependence between the various parameters for the carbonate system in the aqueous phase. These plots are called Deffeyes type diagrams. Deffeyes (1965) first recognized the linearity of pH with respect to Alkalinity and C_T, and Acidity and C_T as co-ordinate axes. However, we have found that pH, with Alkalinity and Acidity as the axes parameters, is the more useful diagram in practical application.

The Deffeyes type plot shown in Fig 4.6 clearly shows that measurement of any two independent parameters completely defines the values for the remaining ones. For example, in Fig 4.6 if pH and Alkalinity are measured, then lines representing these values intersect at a point (termed the aqueous phase equilibrium point) and the values of the remaining parameters can be read off the appropriate ordinates. When zero HCO_3^- alkalinity titration is obtained (which will happen if the water pH ≈ 8,3), then this value together with pH are inadequate for defining an aqueous equilibrium state point because the zero HCO_3^- alkalinity (or HCO_3^- acidity) line does not intersect the pH line (both lines lie on top of each other). Consequently no further information on the system can be derived.

From a practical point of view the Deffeyes type plot supplies the means for estimating chemical dosages to adjust a water from some initial condition (defined say by an Alkalinity and a pH value) to some final condition (defined say by a final Alkalinity and pH value). This arises because changes in the values of the mass parameters with chemical dosing are stoichiometric. (Examples of use are given in Chapter 5).

The Deffeyes type diagram constitutes a single aqueous phase equilibrium diagram. That is, a point in the diagram defines equilibrium between species in the aqueous phase. From the diagram it is not possible to predict quantitatively or qualitatively the propensity for the water either to exchange CO_2 with a gas phase (say air), or to precipitate or dissolve a carbonate mineral (say calcite) in the solid phase. Although the Deffeyes plot is restrictive in this respect, it nevertheless has wide utility because often in evaluating chemical dosing or chemical quality, the reactions take place in the aqueous phase only.

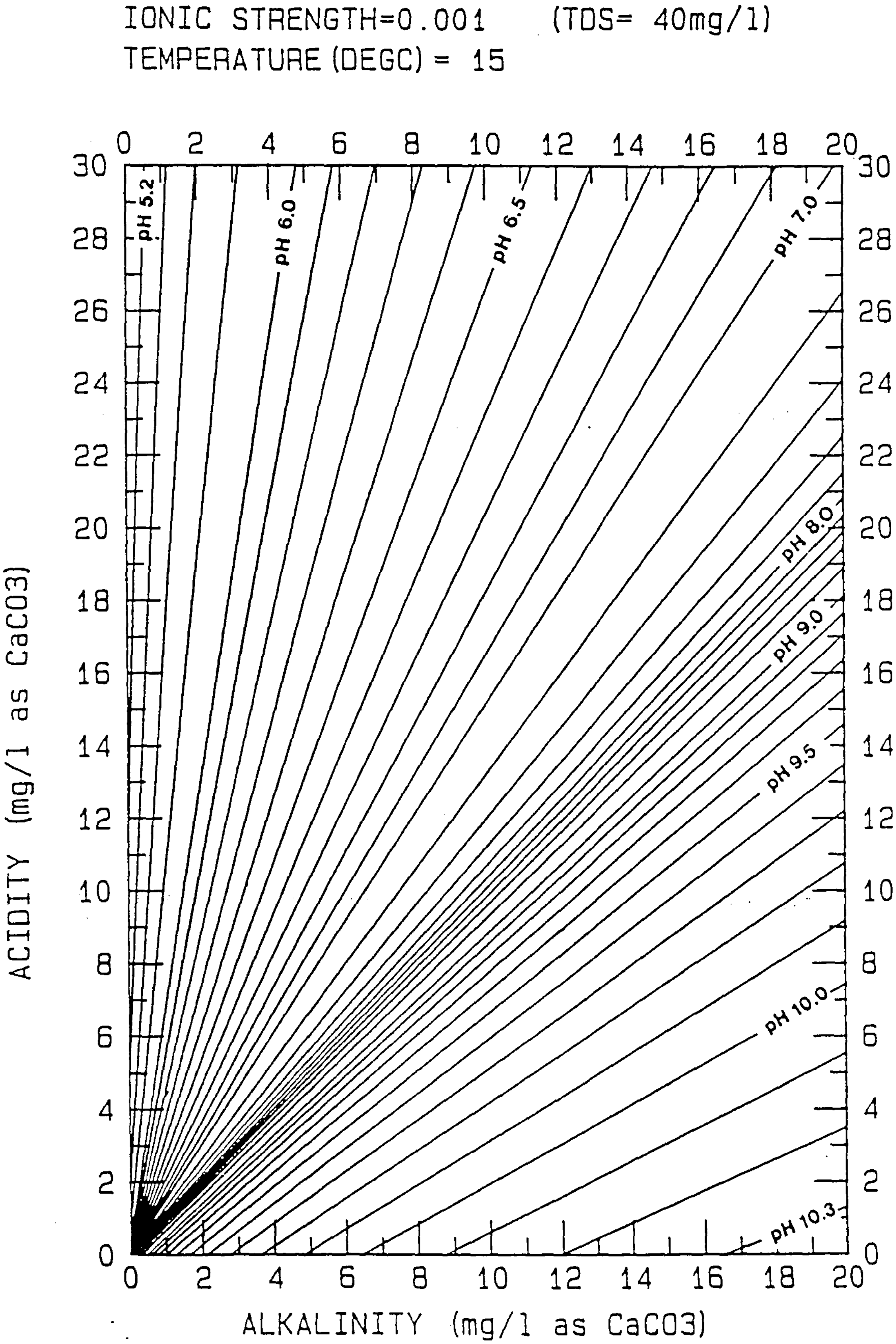

Fig 4.5 Plot of pH lines with Alkalinity and Acidity as axes parameters constitutes a Deffeyes type diagram.

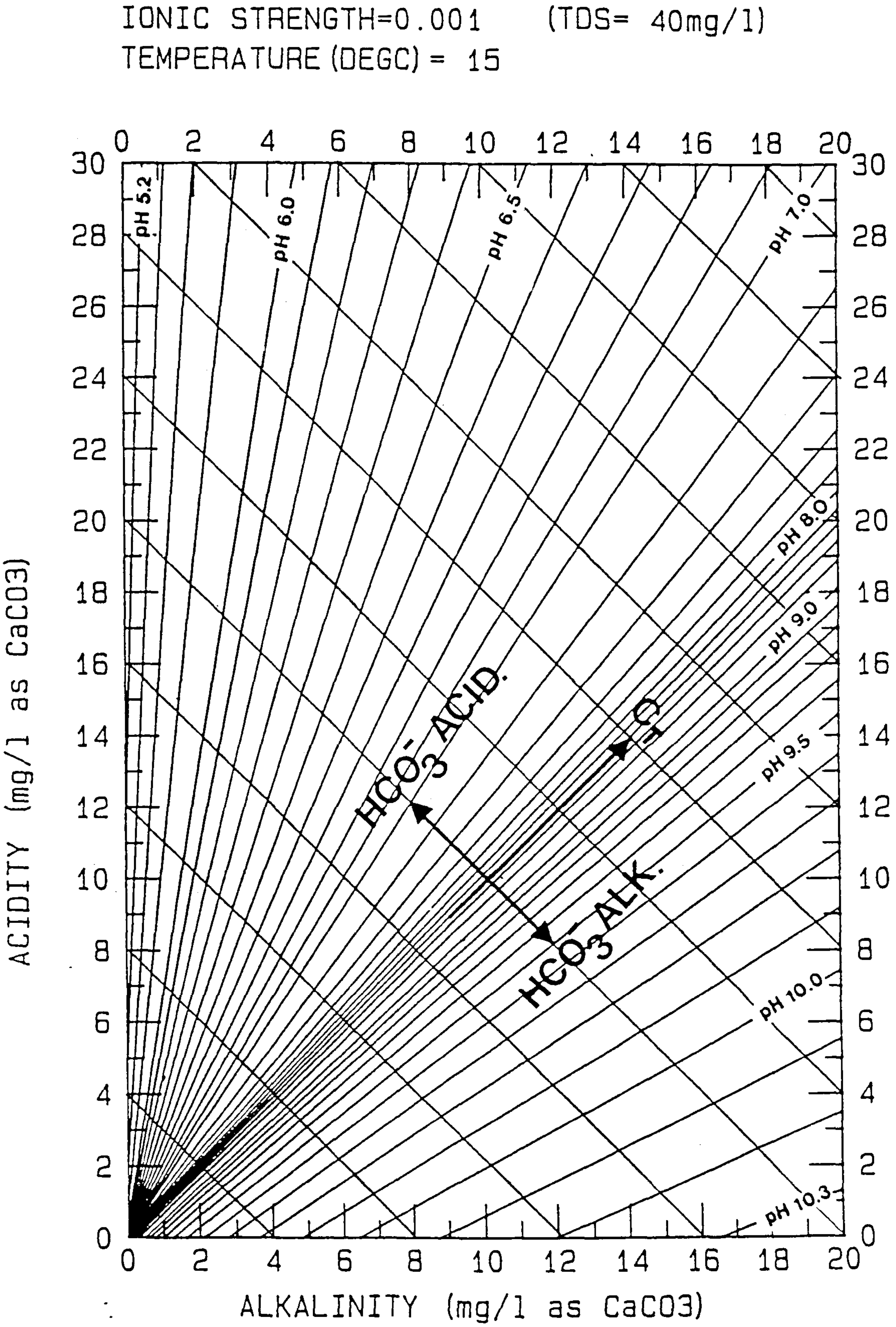

Fig 4.6 General graphical description of interdependence between parameters for the carbonate system for single aqueous phase equilibrium.

In Appendix A are listed a number of single aqueous equilibrium diagrams covering the range of ionic strengths (TDS) and temperatures likely to be encountered in the stabilization of terrestial waters, i.e. ionic strength from 0,001 to 0,01, for temperature from 10 to 25°C.

4.2.6 Practical choice of mass parameter for characterizing the carbonate system in the aqueous phase

In the preceding section it was shown that values for two independent parameters need to be known in order to characterize the carbonate system. Usually pH constitutes one of these because measurement of this parameter can be carried out accurately and quickly via a pH meter and probes standardized against NBS standard buffers. The remaining parameter will be either the total carbonate species concentration, C_T, or one of the various forms of alkalinity or acidity.

C_T can be measured by means of the inorganic carbon analyser. The analyser has the merit that it gives a measure only of the carbonate ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) species. This is not necessarily the case when acidity and alkalinity measurements are made; these always include the H^+ and OH^- species. The analyser in consequence is useful in isolating the carbonate system in waters such as anaerobic digester liquids which also contain weak acid-base systems due to short chain fatty acids, ammonia and phosphate. These substances can cause considerable error when the carbonate system is characterized solely from alkalinity and acidity measurements based on the carbonate species endpoints.

Determination of total inorganic carbonate species concentration using the carbon analyser has the following disadvantages: The analyser, at present, is an expensive instrument requiring specialist staff to operate so that only the larger laboratories can afford and maintain one. Furthermore, because the analyser is sited in a laboratory, the C_T measurement cannot be made in the field.

With regard to the practicality of measurement of the various forms of alkalinity and acidity, each of these is considered below.

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

Procedures for measuring Alkalinity ($H_2CO_3^*$ alkalinity) depend on either colorimetric or potentiometric methods. These involve identification of the titration endpoint pH (equivalence point). The difficulty associated with these is that the $H_2CO_3^*$ equivalence point depends strongly on the total carbonate species concentration which is unknown. Despite this apparent difficulty procedures have been developed whereby one can select the endpoint pH (or appropriate colour change point) with sufficient accuracy provided the Alkalinity is greater than about 30 mg/ℓ as $CaCO_3$ (Standard Methods, 1985). For waters with lower Alkalinity the accuracy arising from this procedure is inadequate; yet for these waters the Alkalinity must be determined with very high accuracy for the following reason: the Alkalinity, with the pH measurement, is used to determine Acidity, a parameter crucial to chemical dosing calculations in water stabilization. In natural low Alkalinity waters, (usually also having low pH of 6 or less), the Alkalinity might be only 2 mg/ℓ as $CaCO_3$ whereas the Acidity might be 10 mg/ℓ or higher. The Acidity value is derived from Alkalinity and pH (see Eq 4.25) but the relationship is a highly sensitive one in the low Alkalinity region. For example, for water with Alkalinity 2 mg/ℓ (as $CaCO_3$) and pH 5,8, an error in Alkalinity of 1 mg/ℓ (as $CaCO_3$) too high will result in Acidity of about 10 mg/ℓ higher than the true Acidity of 11 mg/ℓ. Fortunately however, highly accurate measurement of Alkalinity can be obtained without recourse to 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 D.

The advantages of alkalinity measurement by titration to the $H_2CO_3^*$ equivalence point are summarized below:

(i) The $H_2CO_3^*$ equivalence point lies in a pH region of very low buffer capacity so that titration errors associated with an incorrect endpoint usually are negligible. However, for low alkalinity waters and where high accuracy is needed, a Gran titration should be used.

(ii) Exchange of CO_2 between the water sample and air does not affect the Alkalinity but it is difficult to determine the Alkalinity accurately if such exchange occurs for it causes the endpoint pH to change. However if the titration is done with smooth stirring at deliberate speed then CO_2 exchange is minimized and the endpoint pH does not change sufficiently to affect the Alkalinity measurement significantly. Note that in order to define the carbonate system as it exists at the point of sampling, the pH must be that at the point of sampling. Measurement of pH of a sample subsequent to the time of sampling may give rise to considerable error in the estimates of the carbonate system parameters Acidity and C_T (and hence of the carbonate species) due to loss or gain of carbon dioxide by the sample.

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

Measurement of alkalinity or acidity by titration 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 usually are negligible. For high accuracy a Gran titration can be carried out as set down in Appendix D.

(ii) The endpoint is virtually independent of C_T and can be identified clearly either as an inflection point in the pH-titration curve, or using phenolpthalein as a colour indicator.

Disadvantages of this measurement are:

(i) For waters with pH close to the HCO_3^- equivalence point, it is not possible to characterize 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 of these two parameters causes relatively large errors in the calculated values for C_T and the other forms of alkalinity and acidity. These errors are magnified the closer the measured pH is to the HCO_3^- equivalence point. When the measured pH is at this equivalence point, the associated alkalinity/acidity is zero and no characterization of the carbonate system is possible. This is shown in Fig 4.5 where lines for pH 8,4 and HCO_3^- alkalinity/acidity equal to zero lie on top of each other so that no equilibrium point is obtained from these two measurements.

(ii) Loss or gain of CO_2 from the air by the sample, either prior to or during titration, causes an error in the measurement equal to the molar mass concentration of CO_2 exchanged. However, if the titration is carried out using smooth slow stirring, CO_2 exchange usually is negligible.

(c) Alkalinity or acidity to the CO_3^{2-} equivalence point:
This measurement by titration is not practical for the following reasons:

(i) 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.

(ii) Not only does the pH of the endpoint change with C_T, but also it 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.

4.2.7 $CaCO_3$ concentration scale

Before dealing with examples on the application of the single phase chart to water conditioning, two factors need to be considered. First, the $CaCO_3$ concentration scale: The usual practice in water stabilization (and softening) is to express concentrations in terms of the $CaCO_3$ scale, i.e. as mg/ℓ expressed as $CaCO_3$. Although this approach is contrary to suggestions by the IUPAC, due to its general usage the $CaCO_3$ concentration scale is adopted in this text and all conditioning charts and calculations are in terms of this scale. Second, changes in the values for mass parameters with chemical dosing: Whereas changes in pH with dosing are complex, being governed by equilibria between the carbonate and water species, the concomitant changes in the mass parameters are stoichiometric and consequently very easily determined, see Section 4.2.8.

The concentration scales in common use in water chemistry are the mass concentration, molar, equivalent and mass $CaCO_3$ equivalent scales; The mass $CaCO_3$ equivalent scale is abbreviated to $CaCO_3$ scale in this text. Conversion between these scales is set out in detail by Loewenthal and Marais (1976). Since this monograph deals predominantly with water stabilization, the concentration scale of interest is the $CaCO_3$ scale. For the purposes of developing and utilizing conditioning charts on the $CaCO_3$ scale it is necessary to convert the equilibria and mass balance equations, Eqs (4.4 to 4.24), from the molar to the $CaCO_3$ scale. However, the required chemical dosages using these charts are now on the $CaCO_3$ scale but the plant controller will apply the chemicals on the mass scale, i.e. 'mass in g of chemical/ℓ'. It is necessary therefore to set out briefly the procedures for conversion from one scale to another.

(a) Conversion between concentration scales

(i) Conversion of mass concentration scale to the molar scale:

If A is expressed in g of A/ℓ (i.e. mass concentration scale), then

$$\text{mmol}/\ell \text{ of A} = \frac{(\text{g of A}/\ell).10^3}{MW_A} \tag{4.26a}$$

where MW_A = molecular weight of substance A in g.

(ii) Conversion of molar scale to the equivalent scale:

If A is expressed in mmol/ℓ (molar scale) then,

$$\text{meq of A}/\ell = (\text{mmol of A}/\ell).n_A \tag{4.26b}$$

where 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 all $Ca(OH)_2$, $H_2CO_3^*$, Na_2CO_3, H_2SO_4 and $CaCO_3$; n = 1 for all NaOH, HCℓ and $NaHCO_3$.

meq = milli equivalents.

(iii) Conversion of equivalent scale to $CaCO_3$ scale:

If A is expressed in meq/ℓ, then

$$\text{mg}/\ell \text{ of A as } CaCO_3 = (\text{meq of A}/\ell).EW_{CaCO_3} \tag{4.26c}$$

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

$= MW_{CaCO_3}/n_{CaCO_3} = 100/2 = 50$

(iv) Conversion of molar scale to $CaCO_3$ scale:

If A is expressed in mol/ℓ, then

$$\text{mg}/\ell \text{ of A as } CaCO_3 = (\text{mol of A}/\ell)n_A.EW_{CaCO_3}.10^3 \tag{4.27}$$

For convenience the factors to be used in converting from the mass and molar scales to the (mg/ℓ as $CaCO_3$) scale for a number of chemicals commonly used in stabilization are listed in Table 4.2 below.

Example: In a water softening calculation it is determined that the lime, $Ca(OH)_2$, dosage is 110 mg/ℓ as $CaCO_3$. Determine the dosage on the mass scale in mg $Ca(OH)_2$/ℓ.

From Eq (4.26c),

$$\text{meq of } Ca(OH)_2/\ell = (\text{mg}/\ell \text{ as } CaCO_3 \text{ of lime})/EW_{CaCO_3}$$

$= 110/50 = 2{,}2.$

and, from Eq (4.26b)

$$\text{mmol of } Ca(OH)_2/\ell = (\text{meq of lime}/\ell)/n_{Ca(OH)_2}$$
$$= 2{,}2/2 = 1{,}1$$

and, from Eq (4.26a)

$$\text{mg of } Ca(OH)_2/\ell = (\text{mmol of } Ca(OH)_2/\ell).MW_{Ca(OH)_2}$$
$$= 1{,}1.74 = 81{,}4 \text{ mg}/\ell.$$

Alternatively, from Table 4.2

$$\text{mg}/\ell \text{ as } CaCO_3 = \text{mg } Ca(OH)_2/\ell.50/37$$

$$\text{i.e. mg } Ca(OH)_2/\ell = \text{mg}/\ell \text{ as } CaCO_3.37/50$$
$$= 110.37/50 = 81{,}4$$

(b) <u>Equilibria and mass balance equations on the $CaCO_3$ scale</u>: Transformation of the various equilibria and mass balance expressions from the molar to the $CaCO_3$ scale is carried out by substituting the molar species form with the $CaCO_3$ species form using Eq (4.27). Conventionally the species concentrations on the $CaCO_3$ scale are depicted <u>without brackets</u>.

<u>Table 4.2</u> Conversion factors for transforming from the mass concentration and molar scales to the (mg/ℓ as $CaCO_3$) scale.

Chemical with concentration X mg/ℓ	Molar scale mmol/ℓ	Equivalent scale meq/ℓ	Parameter	Concentration of parameter mg/ℓ as $CaCO_3$
$Ca(OH)_2$	X/74	X/37	Ca^{2+} or OH^-	X.50/37
CO_2	X/44	X/22	CO_2	X.50/22
Na_2CO_3	X/106	X/53	CO_3^{2-}	X.50/53
$NaHCO_3$	X/84	X/84	HCO_3^-	X.50/84
NaOH	X/40	X/40	OH^-	X.50/40
$CaCl_2$	X/112	X/56	Ca^{2+}	X.50/56
H_2SO_4	X/98	X/49	H^+	X.50/49
HCℓ	X/36	X/36	H^+	X.50/36
$CaCO_3$	X/100	X/50	Ca^{2+} or CO_3^{2-}	X.50/50
$C\ell^-$	X/35	X/35	$C\ell^-$	X.50/35
SO_4^{2-}	X/96	X/48	SO_4^{2-}	X.50/48

For the equilibrium equations,

$$H^+.\ HCO_3^-/H_2CO_3^* = K_1'.2,5.10^4 \tag{4.28}$$

$$H^+.CO_3^{2-}/HCO_3^- = K_2'.10^5 \tag{4.29}$$

$$H^+.OH^- = K_w'.2,5.10^9 \tag{4.30}$$

Where 'no brackets' equals species concentration expressed in mg/ℓ as $CaCO_3$.

For the mass balance expressions,

$$\text{Alkalinity} = CO_3^{2-} + HCO_3^- + OH^- - H^+ \tag{4.31}$$

$$HCO_3^-\text{ alkalinity} = CO_3^{2-}/2 + OH^- - H_2CO_3^*/2 - H^+ \tag{4.32}$$

$$CO_3^{2-}\text{ alkalinity} = OH^- - H^+ - HCO_3^- - H_2CO_3^* \tag{4.33}$$

$$\text{Acidity} = H_2CO_3^* + HCO_3^- + H^+ - OH^- \tag{4.34}$$

$$HCO_3^-\text{ acidity} = H_2CO_3^*/2 + H^+ - CO_3^{2-}/2 - OH^- \tag{4.35}$$

$$H_2CO_3^*\text{ acidity} = H^+ - OH^- - HCO_3^- - CO_3^{2-} \tag{4.36}$$

$$C_T = H_2CO_3^*/2 + HCO_3^- + CO_3^{2-}/2 \tag{4.37}$$

Where 'no brackets' indicates species concentrations expressed in mg/ℓ as $CaCO_3$.

Note that the expressions for the interdependence between the various mass parameters, Eqs (4.18 to 4.24) are independent of the concentration unit, and thus are still valid when developed for species concentrations on the $CaCO_3$ scale. For example, adding Eqs (4.31) and (4.34),

$$\text{Alkalinity} + \text{Acidity} = 2\ C_T$$

which is the same as Eq (4.21) on the molar scale.

4.2.8 Changes in mass parameters with dosing

The mass parameters (C_T and the various forms of alkalinity and acidity) change in a simple stoichiometric manner with the mass concentration of chemical dosage and removal. These stoichiometric changes, on the $CaCO_3$ concentration scale, are as follows:

$$\text{Alkalinity change} = CO_3^{2-}(\text{added}) + HCO_3^-(\text{added}) + OH^-(\text{added}) - H^+(\text{added}) \tag{4.38}$$

$$\text{Acidity change} = H_2CO_3^*(\text{added}) + HCO_3^-(\text{added}) + H^+(\text{added}) - OH(\text{added}) \tag{4.39}$$

$$C_T \text{ change} = H_2CO_3^*(\text{added})/2 + HCO_3(\text{added}) + CO_3^{2-}(\text{added})/2 \tag{4.40}$$

All these concentration changes are in mg/ℓ as $CaCO_3$.

Note that the interdependence of Alkalinity, Acidity and C_T given by Eq (4.21) still is valid in terms of the changes in each of these parameters with dosing, i.e. adding Alk(change), Eq (4.38), and Acidity(change), Eq (4.39), and comparing the sum with C_T(change), Eq (4.40), gives

$$\begin{aligned}\text{Alkalinity(change)} + \text{Acidity(change)} &= CO_3^{2-}(\text{added}) + 2.HCO_3^-(\text{added}) \\ &\quad + H_2CO_3^*(\text{added}) \\ &= 2\ C_T(\text{change}).\end{aligned}$$

The very simple stoichiometric changes in the mass parameters with chemical dosage, utilized in conjunction either with the Alkalinity-Acidity-pH (Deffeyes type) diagram or with the Modified Caldwell-Lawrence diagram (see Section 4.3) forms the basis for predicting chemical dosages in conditioning of water.

4.2.9 Deffeyes type diagram in water conditioning

The Deffeyes type conditioning diagram describes the equilibrium state in the aqueous phase. It can be used in conditioning problems provided these do not involve precipitation, or, CO_2 equilibrium with a gas phase. Examples of its use include: (i) stabilization of Calcium-Alkalinity deficient waters. Here the Deffeyes type diagram forms a vital initial step in establishing the initial Acidity from known Alkalinity and pH values prior to subsequent stabilization using the Caldwell-Lawerence diagram; initial Acidity estimation in the Caldwell-Lawrence diagram for Calcium-Alkalinity deficient waters ($Ca^{2+} < 10$; Alk < 5 both in mg/ℓ as $CaCO_3$ and pH $< 6{,}5$) is not practical because this requires inordinately extended plot limits, (ii) water blending wherein it is presumed that during the blending stage no $CaCO_3$ precipitation or CO_2 exchange with air occur, and (iii) chemical conditioning using the Lawson-Snyders process wherein mineral acid is added to the influent water and the acidified water is passed through limestone ($CaCO_3$) in a manner such that any CO_2 released is redissolved by the water, Lawson and Snyders (1962) and Mills and Loewenthal (1984).

Utilization of the Deffeyes type diagram is based on the observation in Section 4.2.4 that if values are known for any two independent parameters for the system, then values for the remaining parameters can be determined from theory. Generally, Alkalinity and pH are the two parameters most conveniently measured and hence usually are used to define the chemical state of a water. The change in this state with chemical dosing is then determined in the equilibrium diagram as follows:

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

(ii) The new Alkalinity and Acidity values are determined from the mass concentration of chemical added (or removed) using Eqs (4.38 and 4.39) respectively.

(iii) The new pH is determined by plotting the lines representing the new Alkalinity and Acidity values [determined in (ii) above] in the diagram; these lines intersect at a point and the new pH is the value for the pH line through this intersection point.

These three steps constitute the general pattern of solution to most types of conditioning problems. Examples on applications of these steps in the Deffeyes diagram for a range of water conditioning problems are set out in detail by Loewenthal and Marais (1976). However, for dosage estimation in water stabilization the diagram usually is not particularly useful (other than its application to Calcium-Alkalinity deficient waters outlined above) because it does not provide the means for assessing the $CaCO_3$ saturation state and changes in this state with dosing - a crucial aspect to stabilization. For these purposes the Modified Caldwell-Lawrence diagram was developed and is considered in the following section.

4.3 SOLID-AQUEOUS PHASE EQUILIBRIUM

With precipitation or dissolution of a mineral there is a reaction between the species in the solid phase and corresponding species in solution. Precipitation and dissolution are the net results of precipitation and dissolution reactions occurring concurrently, when, with the former, precipitation rate exceeds the dissolution rate, and with the latter the dissolution exceeds the precipitation rate. As the reaction proceeds, there is a decreasing difference between the two concurrent rates until the two are equal and no net precipitation or dissolution occurs. The equality in rates defines the equilibrium state and is formulated in terms of the solubility product equation.

For the carbonate system, softening involves two mineral precipitants, calcite ($CaCO_3$) and $Mg(OH)_2$. The solubility product equations are respectively

$$[Ca^{2+}][CO_3^{2-}] = K_{sp}/f_D^2 = K'_{sp} \qquad (4.41)$$

and

$$[Mg^{2+}][OH^-]^2 = K_{spm}/f_D \cdot f_M^2 = K'_{spm} \qquad (4.42)$$

where f_D, f_M = activity coefficient for divalent and monovalent species respectively.

K_{sp}, K_{spm} = thermodynamic solubility product constants for calcium carbonate and magnesium hydroxide respectively, the values of which depend on temperature.

K' = apparent solubility product constant.

The thermodynamic solubility product constants K_{sp} and K_{spm} in Eqs (4.41 and 4.42) vary with temperature as follows:

(i) For $K_{sp}(CaCO_3)$ in the range 0°C to 80°C, from Loewenthal and Marais (1976),

$$pK_{sp} = 0{,}01183t + 8{,}03 \qquad (4.43)$$

(ii) for $K_{spm}(Mg(OH)_2)$ in the range 0°C to 80°C from Hamer (1961),

$$pK_{spm} = 0{,}0175t + 9{,}97 \qquad (4.44)$$

where t is in degC.

The activity coefficients in Eqs (4.41 and 4.42), to calculate K'_{sp} and K'_{spm}, are readily estimated for low salinity waters for a known ionic strength or TDS as set out in Section 2.1, Chapter 2. Thus, for the solubility product equations, Eqs (4.41 and 4.42), if the temperature and ionic strength are known, the apparent constants K'_{sp} and K'_{spm} can be determined.

Referring to the solubility product equations, Eqs (4.41 and 4.42), if the left hand side exceeds the right hand side then precipitation of the solid will occur until the two sides are equal. If the left hand side is less than the right hand side, then, if the solid mineral is present, dissolution will occur until equalibrium again is attained; if the mineral is not present, no dissolution can occur, equilibrium with respect to the mineral cannot be attained and the solubility product equation does not apply, i.e. the solution remains undersaturated.

The rates of precipitation and dissolution are slow compared to the rates at which equilibrium are attained between dissolved carbonate species and the water species. In many instances the precipitation rate is so slow that for practical purposes the dissolved species concentrations can be accepted to remain unaffected in the supersaturation state for long periods of time. So, for example, although water usually is discharged to distribution systems in a slightly supersaturated state, no detectable precipitation is observed prior to distribution. (In softening a large mass of solids in a finely divided state, a slurry, is mixed with the supersaturated solution so that the surface area of solid is so large that the rate of precipitation from the supersaturated solution is increased by one or more orders of magnitude compared with the precipitation rate when no slurry is present. The effluent from such a softening unit usually can be assumed to have no residual potential for precipitation provided there is no CO_2 transfer between the water body and the atmosphere).

The state of over or undersaturation can be expressed in a number of ways including the (i) Langelier Saturation Index, SI and (ii) calcium carbonate precipitation potential. The Langelier Saturation Index is the difference between the pH measured in a water and the pH_s that a water should have to be just saturated for the Alkalinity and calcium concentrations measured. The calcium carbonate precipitation/dissolution potential defines the mass of $CaCO_3$ that must precipitate or dissolve to bring the water to a saturated condition (the potential is measured in practice by the Marble test, Standard Methods, 1985).

4.3.1 Langelier Saturation Index (SI)

From theoretical considerations Langelier (1936) developed a 'saturation index' which, by its sign establishes the state of a water with respect to over- or undersaturation with respect to $CaCO_3$. The Langelier Saturation Index, SI, is defined as ($pH_{actual}-pH_s$) and is negative for undersaturation and positive for supersaturation, valid only in the normal pH regions pH $\lesssim$ 9,5. Determination of SI from measurements of pH and Alkalinity and calcium concentrations is carried out as follows:

$$SI = pH_{actual} - pH_s$$

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 $6 < pH < 9$,

$pH_s \approx pK_2' - pK_s' + p[Alkalinity] + p[Ca^{2+}]$

[ ] = molar concentration

K_2' and K_s' = apparent equilibrium constants as defined in Eqs (4.10 and 4.41) respectively.

Langelier emphasized that the Index must be considered only as a qualitative measure of over- or undersaturation. This point has not always been appreciated and waters are often conditioned, say, to give a positive SI of +0,3 and this value interpreted as if it is related directly to both the mass of $CaCO_3$ expected to deposit in a pipe system and the pacifying properties of water to aggressive and corrosive reactions. However, a positive SI guarantees neither of these:

> The pH change to saturation, when $CaCO_3$ precipitates from a supersaturated water, does not equal the SI value. The reason is that all the parameters Alkalinity, Ca^{2+} concentration and pH change with precipitation so that the actual change in pH will vary depending on the initial values for these three parameters. This is illustrated in Table 4.3 in which is listed the mass of $CaCO_3$ to be precipitated to saturation for a number of waters each with SI = 0,3 but with varying Alkalinity, Ca^{2+} and pH values.
>
> Referring to Table 4.3, two important conclusions can be drawn: First, the values for SI and precipitation potential are not interrelated. For example, the water with pH 7,3 (and SI = +0,3) has a precipitation potential of 35 mg/ℓ and is likely to give rise to extensive scaling in pipes conveying the water with possible pipe narrowing. In contrast, the water with pH 8,4 (and SI = +0,3) has a $CaCO_3$ precipitation potential of only 2 mg/ℓ which is below the value recommended in Section 2.2 for passivation of aggressive reactions to cement material. Second, a positive SI does not guarantee that either or both Alkalinity or/and calcium concentration have values greater than the minima recommended in Section 3.5 for corrosion passivation. This is illustrated in Table 4.3 for the two waters with pH values 9,0 and 9,3, for which Alkalinity and/or Ca^{2+} concentrations are less than the recommended value of 50 mg/ℓ as $CaCO_3$.

In conclusion, a positive SI value on its own guarantees only supersaturation with respect to $CaCO_3$. The index does not relate to any of the quantitative criteria for water stabilization set out in Sections 2.2 and 3.5.

4.3.2 Calcium carbonate precipitation/dissolution potential

The precipitation/dissolution potential defines the mass of $CaCO_3$ to be precipitated from, or dissolved into, a water to attain saturation with respect to $CaCO_3$. This parameter therefore gives both a qualitative and quantitative description of the saturation state, and serves as a useful parameter in setting quality criteria in water stabilization (see Sections 2.2 and 3.5).

Table 4.3: 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

Principally two problems arise in the practical application of the precipitation potential to water stabilization. First, although the chemical state (and precipitation potential) is fixed for reported values of Alkalinity, calcium concentration and pH, there is no simple method for determining the precipitation/dissolution potential from these three values because it is not possible to formulate an explicit equation for the potential in terms of Alkalinity, calcium concentration and pH. Consequently, the magnitude of the potential has to be determined by some numerical method of successive approximation which is both complex and time consuming. Second, calculations for water stabilization require determination of the masses and types of chemical dosages, to be applied prior to distribution of a water, to adjust Alkalinity, calcium concentration and pH such that the water has inter alia a prescribed precipitation potential. However, the intricate interdependence between chemical dosing and the precipitation potential make such calculations exceedingly complex and are not practical if computer facilities are not available.

Recognizing that numerical methods are impractical for determination of both the precipitation potential and chemical dosages required for stabilization, practical approaches have been developed using graphical plots for rapid solution to these types of problems. The most useful of these plots is the Modified Caldwell-Lawrence (MCL) diagram.

4.4 MODIFIED CALDWELL-LAWRENCE (MCL) DIAGRAM

The MCL diagram is a multi-phase equilibrium diagram for carbonate species in the aqueous, solid ($CaCO_3$) and gas (carbon dioxide) phases. The diagram has co-ordinate parameters Acidity and (Alkalinity-calcium) and is made up of families of curves representing (a) pH and Alkalinity (for equilibrium between species in the aqueous phase), and (b) Ca^{2+} values at saturation with respect to $CaCO_3$ (for equilibrium between species in the aqueous and solid phases). A typical diagram is shown in Fig 4.7.

The theory for constructing the MCL diagram is set out in detail by Loewenthal and Marais (1976). The aqueous phase equilibria depicted by linking Alkalinity, Acidity and pH in the MCL diagram are identical to those in the Deffeyes type diagram, but because of the axes chosen for the MCL plot, linear presentation is lost.

The great advantage of the MCL diagram is that lines representing the calcium concentration, to give saturation with respect to $CaCO_3$, are superimposed on the diagram. Consequently, the value of the Ca^{2+} line through the intersection point of lines representing measured pH and Alkalinity (or pH and Acidity, or Alkalinity and Acidity) defines the Ca^{2+} value for saturation. If the line representing measured Ca^{2+} does not cross the intersection point of the observed pH-Alkalinity intersection then a condition of either under or supersaturation is defined from which the potential for dissolution or precipitation can be derived. Thus, in the MCL diagram one can deal with a water considering the aqueous phase only, as in stabilization, or the aqueous and solid phases, as in softening. In addition, by superimposing partial pressure lines for CO_2, one can deal with aqueous-solid-gas phases or aqueous-gas phases, arising in CO_2 stripping or absorption (see Section 4.5 below). Procedures for solving problems in the aqueous, aqueous-solid, aqueous-gas and aqueous-solid-gas phases are set out in Chapter 5.

4.5 EQUILIBRIUM BETWEEN CO_2 IN THE AIR AND CARBONATE SPECIES IN SOLUTION.

The in situ dissolved CO_2 content of underground waters usually is very high compared with waters in contact with the air. When pumped to surface and exposed to air, the difference in partial pressure between air and water induces a state of CO_2 supersaturation in the water and CO_2 is expelled. This causes the pH to increase, and, depending on the calcium content of the water, the apparent solubility product for $CaCO_3$ may be exceeded causing precipitation; this may give rise to severe scaling problems in conduits carrying the water. To prevent such precipitation problems arising, it is necessary to be able to predict, from analyses of the water, the potential for CO_2 loss and consequential $CaCO_3$ precipitation potential.

Prediction of these values can be rapidly carried out using the MCL diagram. However, this requires superimposing on the diagram a line representing equilibrium between carbonate species in solution and CO_2 in the air. The theory for plotting such a line is dealt with briefly below.

4.5.1 <u>Interpretation of aqueous-gas phase equilibrium in the MCL diagram.</u>

Carbon dioxide exchange between water and the atmosphere takes place until the CO_2

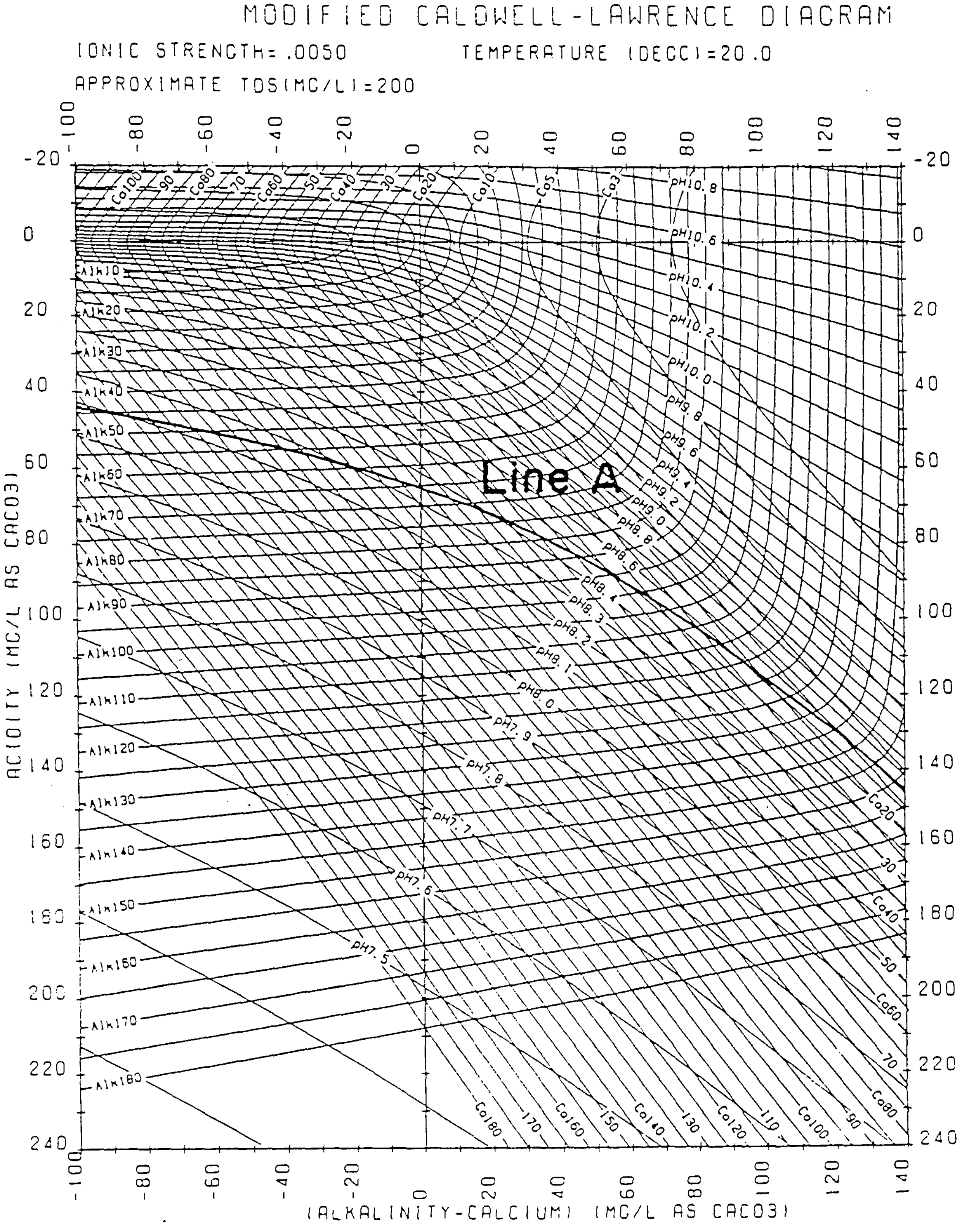

Fig 4.7 Modified Caldwell Lawrence diagram. Line A represents CO_2 equilibrium with the air.

partial pressures 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 equilibrium, the pH in the water changes and there is a redistribution of the dissolved carbonate species concentrations, i.e. a change in the dissolved CO_2 concentration occurs and more CO_2 is exchanged with the air. Exchange of CO_2 between air and water does not change the Alkalinity only Acidity and pH provided no $CaCO_3$ precipitation occurs. The pH at which equilibrium is established depends on the Alkalinity of the water and the partial pressure of CO_2 in the gas phase.

The rate of CO_2 transfer depends on the difference in partial pressure of CO_2 across the air-water interface. With mixing, surface renewal of CO_2 over- or undersaturated water at the interface increases the transfer rate. In tranquil bodies of water CO_2 equilibrium between air and water may be attained only at the water-air interface and chemical changes in the body of water will be controlled by the rate of diffusion of the CO_2 to the surface.

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 plus carbonic acid, $H_2CO_3^*$, is defined by Henry's Law as

$$[H_2CO_3^*] = K_{CO_2} \cdot \bar{p}_{CO_2} \qquad (4.45)$$

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

From data supplied by Hamer (1961), a relationship linking K_{CO_2} to temperature in degrees Kelvin in the range 273K to 343K (0°C to 70°C) is

$$pK_{CO_2} = - 1760{,}0/T + 9{,}619 - 0{,}00753T \qquad (4.46)$$

where T is in degrees Kelvin.

The link between Alkalinity and pH for a constant partial pressure of CO_2 is developed as follows:

From Eq (4.11)

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

Solving for $[CO_3^{2-}]$ and $[HCO_3^-]$ from Eqs (4.5 and 4.6) respectively and substituting into the equation above for Alkalinity,

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

and, substituting for $[H_2CO_3^*]$ from Eq (4.45),

$$\text{Alk} = \bar{p}_{CO_2} \cdot K_{CO_2} \cdot 10^{pH-pK_1'}\ (2.10^{pH-pK_2'}+1) + 10^{pH-pK_w'}-10^{-pH}/f_m \qquad (4.47)$$

Thus, from Eq (4.47), Alkalinity is related to pH for a water at equilibrium with respect to some CO_2 partial pressure in the gas phase.

Equilibrium between carbonate species in the aqueous phase and CO_2 in the gas phase (say air with $\bar{p}_{O_2}$ = 0,00032 Atm) can be depicted in the MCL diagram as follows:

(i) For water with some prescribed temperature and ionic strength determine values for the apparent constants, K_1' and K_2' and K_w' (as set out in Section 4.2) and for K_{CO_2} from Eq (4.46).

(ii) For a range of pH values (and $\bar{p}_{CO_2}$ = 0,00032 Atm) determine the corresponding Alkalinity values using Eq (4.47).

(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 Fig 4.7. That is, if the aqueous phase equilibrium point in the diagram (determined from any pair of known values for Alkalinity, Acidity and pH) occurs on Line A, then the water is also in equilibrium with CO_2 in the air. If not, then CO_2 is expelled or taken up by the water until two-phase equilibrium condition is attained.

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Chapter 5

Application of Conditioning Diagrams to Stabilization and Softening Problems

5.1 INTRODUCTION

Stabilization problems involve calculating the chemical dosages to adjust the chemical state of a water (condition the water) to meet the guidelines set out in Sections 2.4 and 3.4. That is

(i) Alkalinity and calcium concentrations each to exceed about 50 mg/ℓ as $CaCO_3$, and a pH in the range $6,5 < pH < 9,5$.

(ii) the water to be supersaturated with respect to calcium carbonate with a precipitation potential of about 4 mg/ℓ $CaCO_3$;

(iii) the ratio $(C\ell^- + SO_4^{2-})$/Alkalinity $\lesssim 0,2$ (where species concentrations are expressed on the equivalent scale); and/or the concentrations of each Cl^- and SO_4^{2-} must not exceed 50 mg/ℓ (corrosion protection guideline);

(iv) the sulphate species concentration to be less than about 350 mg SO_4^{2-}/ℓ (aggression protection guideline);

(v) the dissolved oxygen concentration should be greater than about 4 mg/ℓ.

All the guidelines usually can be satisfied by appropriate chemical addition and aeration. However, satisfaction of guideline (iii) may not be practicable if either or both of the SO_4^{2-} and $C\ell^-$ concentrations are high, because either the chemical dosing costs are too high, or the water will be too hard after stabilization. In that event, because this guideline is relevant to the termination of corrosion of mild steel and cast iron conduits (see Section 3.4, Chapter 3) it might be necessary to use concrete, asbestos cement and/or plastic pipes, or to line metal pipes with inert plastics, resins or cement.

Softening problems involve calculating the chemical dosages to reduce the calcium and magnesium concentrations in the water to acceptable values. Chemical conditioning of water for general distribution falls into four categories, those concerned with waters having

(1) adequate calcium and Alkalinity,
(2) calcium and carbonate species deficiency,
(3) excessive (high) calcium and magnesium concentrations, and
(4) excessive dissolved carbon dioxide with high calcium and magnesium concentrations.

In the rest of this chapter the conditioning and stabilization of these categories of water will be discussed in detail, using the Modified Caldwell-Lawrence (MCL) and Deffeyes diagrams both to assess water quality and to select the most appropriate chemical treatment method and chemical dosage type(s). These are illustrated by worked examples.

For all the examples presented, before any assessment can be carried out it is necessary to determine by measurement the relevant physical and chemical characteristics of the water to be investigated. In conditioning and stabilization this comprises determination of

(a) Temperature: This is determined in situ or immediately after drawing of water sample; maximum and minimum yearly temperatures are required.

(b) Total inorganic dissolved solids: Found from a standard test, and used to estimate ionic strength approximately (Standard Methods, 1985, and see Chapter 2, Section 2, Eq 2.6).

(c) Calcium concentration: Found from the standard chemical test (Standard Methods, 1985).

(d) Carbonate system parameters: Usually these are Alkalinity and pH; it was shown in Chapter 4 that from practical considerations these are the two most useful parameters to measure (Standard Methods, 1985, and Chapter 4, Section 2).

5.2 STABILIZATION OF WATERS WITH ADEQUATE CALCIUM AND ALKALINITY

In this category waters have Alkalinity and Ca^{2+} values that satisfy the minimum criteria set out in Section 5.1, i.e. both Alkalinity and Ca^{2+} values are greater than 50 mg/ℓ as $CaCO_3$; the pH is already in the region acceptable for general distribution (i.e. $6{,}5 \lesssim pH \lesssim 9{,}5$). Provided the $(C\ell^- + SO_4^{2-})$/Alkalinity ratio is not a limiting factor and the water is well oxygenated, it is necessary only to ensure a slightly supersaturated state (with a $CaCO_3$ precipitation potential of about 4 mg/ℓ) to deliver a water satisfying all the criteria for stabilization. Many of the inland waters in South Africa fall into this category.

The solution procedure requires (a) an assessment of the $CaCO_3$ saturation state, and (b) if necessary, modification of this state by chemical conditioning to that of prescribed supersaturation.

5.2.1 Assessment of the initial saturation state

Assessment of the initial state is carried out in the following steps:

(i) Select the Modified Caldwell-Lawrence diagram from those listed in Appendix B with ionic strength and temperature equal to (or close to) those for the water to be stabilized.

(ii) Sketch in the diagram the lines representing the measured values for pH, Alkalinity and Ca^{2+} for the raw water.

(iii) Identify the point in the diagram representing equilibrium between species in the aqueous phase, termed the aqueous phase equilibrium point. It is given by the intersection point of the lines representing the measured pH and Alkalinity values of the raw water.

(iv) Determine the Acidity of the raw water: This is given by the Acidity ordinate value of the aqueous phase equilibrium point, that is, the Acidity ordinate value of the point of intersection of lines representing measured pH and Alkalinity values.

(v) Estimate qualitatively the saturation state of the water: This is determined by comparing the actual (measured) Ca^{2+} value with the theoretical saturated Ca^{2+} value for the measured Alkalinity and pH values. The theoretical saturated Ca^{2+} value is given by the value of the Ca^{2+} line through the aqueous phase equilibrium point. If this Ca^{2+} value is greater than the measured value, the water is undersaturated; if less the water is supersaturated; and, if equal, the water is just saturated, - a water is just saturated with respect to $CaCO_3$ when the lines representing measured Alkalinity, pH and Ca^{2+} all intersect at the aqueous phase equilibrium point in the diagram.

(vi) Determine the potential mass concentration of $CaCO_3$ to be dissolved or precipitated to saturation: This determination is based on basic behaviour of $CaCO_3$ dissolution/precipitation, that when $CaCO_3$ precipitates or dissolves both coordinate parameters Acidity* and (Alkalinity-Ca^{2+})* of MCL diagrams remain constant, (Section 4.2.8, Chapter 4). In the Modified Caldwell-Lawrence diagram, constant Acidity is given by the horizontal line through the aqueous phase equilibrium point; constant (Alkalinity-Ca^{2+}) by the vertical line through the intersection of the lines representing the measured Alkalinity and calcium values, or equivalently by the vertical ordinate value defined by the measured (Alkalinity-Ca^{2+}) value.

The intersection point of the vertical and horizontal lines defines the pH, Alkalinity and calcium values for which this water will be just saturated with respect to $CaCO_3$, by dissolving or precipitating $CaCO_3$. That is, for a water just saturated, lines representing pH, Alkalinity, calcium, Acidity and (Alk-Ca) all intersect at a single point termed the aqueous-solid phase equilibrium point.

(vii) The potential mass concentration of $CaCO_3$ to be precipitated or dissolved to saturation is given by the difference between the measured Alkalinity (or calcium) and the Alkalinity (or calcium) lines through the solid-aqueous phase equilibrium point - both Alkalinity and calcium change by equal amounts with dissolution or precipitation of $CaCO_3$.

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*In the text abbreviations will be used for Acidity and (Alkalinity-Ca^{2+}), i.e. Acid and (Alk-Ca) respectively.

EXAMPLE 1 - Assessment of initial state - Supersaturated water

Analyses of a water gives Alkalinity 80 mg/ℓ, Ca^{2+} = 100 mg/ℓ (both as $CaCO_3$), pH 8,6, ionic strength 0,005 (TDS = 200 mg/ℓ), and T = 20°C. Determine the saturation state of the water and the mass concentration of $CaCO_3$ which potentially can precipitate from the water.

Solution

(i) Modified Caldwell-Lawrence diagram (MCL diagram):

Select the MCL diagram from those listed in Appendix B with μ = 0,005 and T = 20°C, see Fig 5.1.

(ii) Determine Acidity of the water:

Identify, or plot by interpolation, the lines representing the measured Alkalinity, Ca^{2+} and pH values. The aqueous phase equilibrium point is given by the intersection point of lines representing pH 8,6 and Alkalinity 80 mg/ℓ, Point 1 in Fig 5.1. Acidity ordinate value of Point 1 defines the initial Acidity of the water, 77 mg/ℓ as $CaCO_3$.

(iii) $CaCO_3$ saturation state:

The lines representing measured Alkalinity, Ca^{2+} and pH values do not intersect in a single point, consequently, the water is either under- or supersaturated with respect to $CaCO_3$. The Ca^{2+} to give saturation for Alkalinity 80 mg/ℓ and pH 8,6 is the value of the Ca^{2+} line through the aqueous phase equilibrium point, Point 1, i.e. Ca^{2+} 30 mg/ℓ. The measured Ca^{2+} concentration is 100 mg/ℓ. As the theoretical Ca^{2+} value for saturation (30 mg/ℓ as $CaCO_3$) is less than the measured value (100 mg/ℓ as $CaCO_3$), the water is supersaturated.

(iv) Potential mass concentration of $CaCO_3$ to be precipitated to saturation:

As the water is supersaturated, precipitation of solid $CaCO_3$ will take place until saturation is achieved. The mass concentration that will precipitate is found as follows:

Saturation is given by the aqueous-solid phase equilibrium point in the diagram, by the intersection of the lines representing Acidity and (Alk-Ca). Draw in the horizontal line representing Acidity 77 mg/ℓ. Determine (Alk-Ca), i.e. (80-100) = -20 mg/ℓ, and draw in the vertical line (Alk-Ca) = -20 (alternatively, the intersection point of lines for Alkalinity 80 mg/ℓ and Ca 100 mg/ℓ in fact defines (Alk-Ca) = -20, i.e. a vertical line through Point 2 gives (Alk-Ca) = -20. Aqueous-solid phase equilibrium point is established by the intersection of the ordinate values Acidity = 77 mg/ℓ and (Alk-Ca) = -20 mg/ℓ, i.e. Point 3.

After precipitation of $CaCO_3$ from the water, the Alkalinity, Ca^{2+} and pH lines through Point 3 are the values at saturation, i.e. Alkalinity 75 mg/ℓ, Ca^{2+} 95 mg/ℓ and pH 8,13.

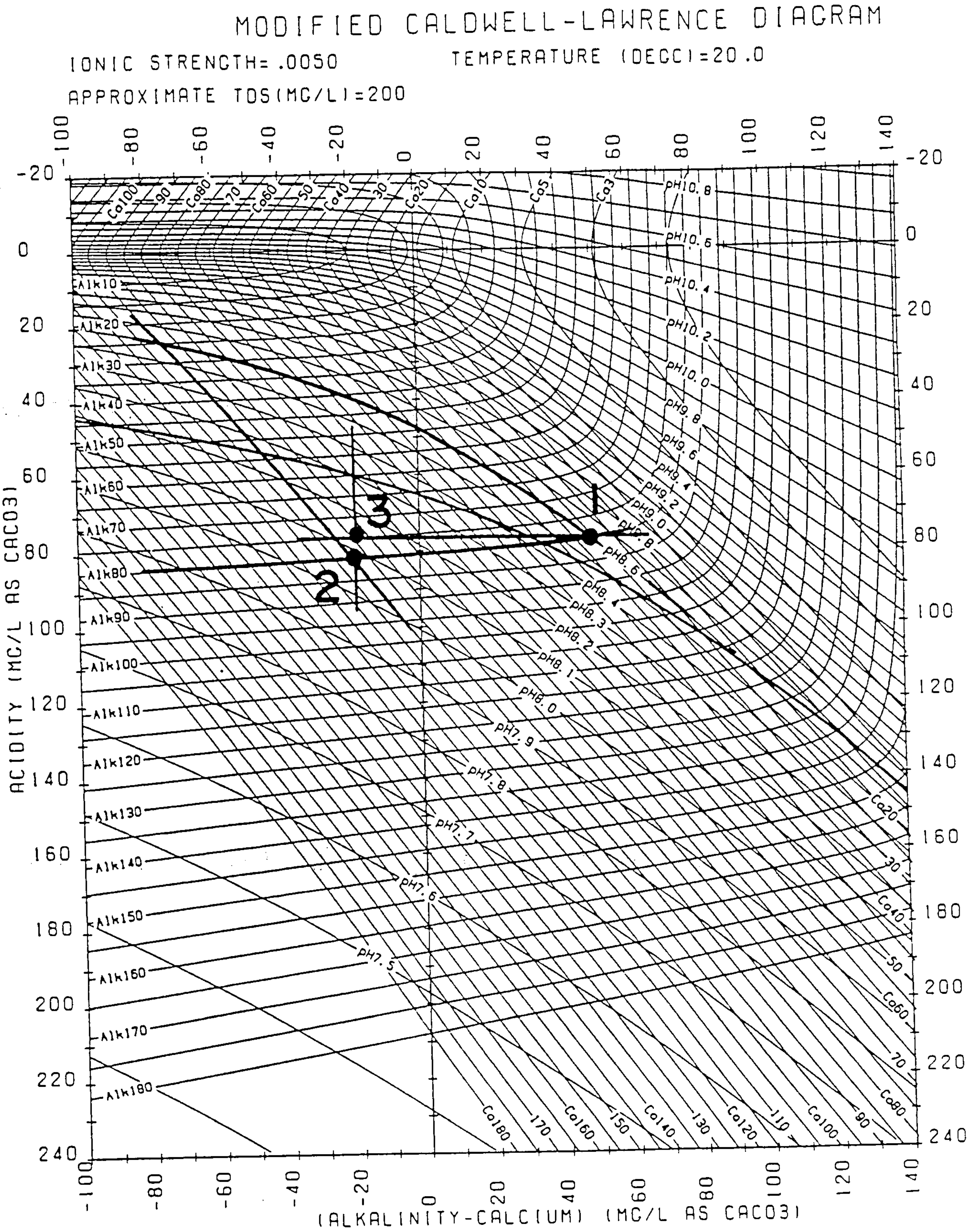


Fig 5.1 Example 1: $CaCO_3$ precipitation potential for a supersaturated water with Alk 80 mg/ℓ, Ca^{2+} 100 mg/ℓ, pH 8,6.

$CaCO_3$ precipitation potential = Alk(initial) - Alk(saturation)
= 80 - 75 = 5 mg/ℓ
= Ca^{2+}(initial) - Ca^{2+}(saturation)
= 100 - 95 = 5 mg/ℓ

EXAMPLE 2: Assessment of initial state - Undersaturated water

Analyses of a water gives Alkalinity 80 mg/ℓ, Ca^{2+} 30 mg/ℓ (both as $CaCO_3$), pH 8,1, ionic strength 0,005 and temperature 20°C. Determine the saturation state of the water and the mass concentration of $CaCO_3$ which potentially can dissolve into the water.

Solution

(i) Modified Caldwell-Lawrence diagram (MCL diagram):

Select the MCL diagram from those listed in Appendix B with μ = 0,005 and T = 20°C, see Fig 5.2.

(ii) Determine the Acidity of the water:

Identify and plot by interpolation the lines representing the measured Alkalinity, Ca^{2+} and pH values. The aqueous phase equilibrium point is given by the intersection point of lines representing pH 8,1 and Alkalinity 80 mg/ℓ, i.e. Point 1. Acidity ordinate value of Point 1 defines the initial acidity of the water, i.e. Acidity = 82 mg/ℓ as $CaCO_3$.

(iii) $CaCO_3$ saturation state:

The lines representing measured Alkalinity, Ca^{2+} and pH do not intersect in a single point, consequently the water is either under or supersaturated with respect to $CaCO_3$. The Ca^{2+} required to give saturation for Alkalinity 80 mg/ℓ and pH 8,1 is the value of the Ca^{2+} line through the aqueous phase equilibrium point, Point 1, i.e. Ca^{2+} 95 mg/ℓ. The measured Ca^{2+} concentration is 30 mg/ℓ. As the theoretical Ca^{2+} value for saturation (95 mg/ℓ) is more than the measured value (30 mg/ℓ), the water is undersaturated with respect to $CaCO_3$.

(iv) Potential mass concentration of $CaCO_3$ to be dissolved to saturation:

If this water was placed in contact with solid $CaCO_3$ (marble test) then the solid will dissolve until saturation is achieved; the mass concentration that will dissolve is determined using the MCL diagram as follows:

Saturation is given by the aqueous-solid phase equilibrium point in the diagram, by the intersection of the lines representing Acidity and (Alk-Ca^{2+}). Draw in the horizontal line representing Acidity 82 mg/ℓ. Determine (Alk-Ca), i.e. (80-30) = 50 and draw in the vertical line with ordinate value 50 mg/ℓ.

Alternatively, the line representing (Alk-Ca) is the vertical line through the intersection point of lines for Alkalinity 80 mg/ℓ and Ca^{2+} 30 mg/ℓ, i.e. vertical line

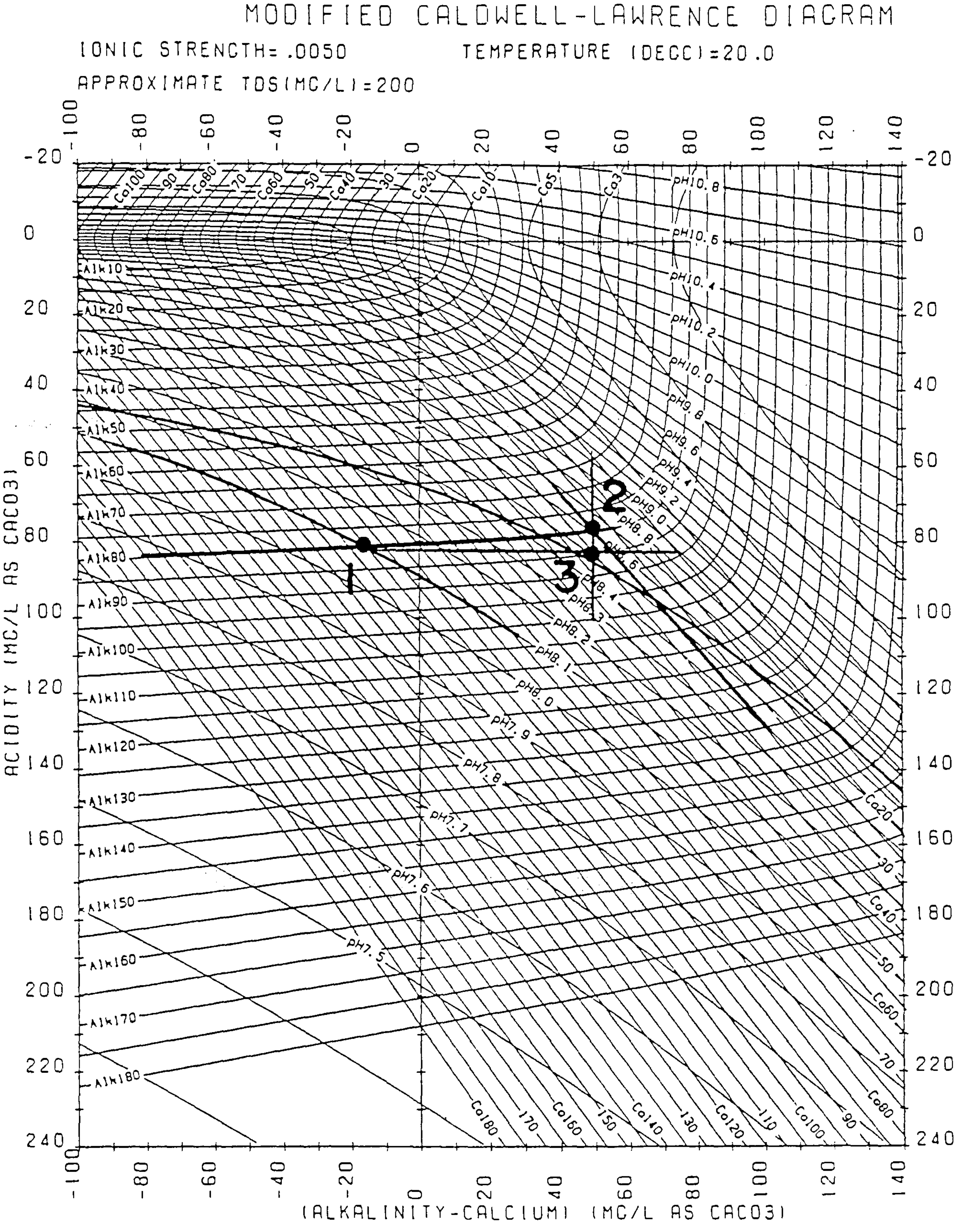


Fig 5.2 Example 2: $CaCO_3$ dissolution potential for an undersaturated water with Alk 80 mg/ℓ, Ca^{2+} 30 mg/ℓ and pH 8,1.

through Point 2 in Fig 5.2 with ordinate value (Alk-Ca^{2+}) = (80 - 30) = 50 mg/ℓ. The aqueous-solid phase equilibrium point is established by the intersection of the ordinates Acidity 82 mg/ℓ and (Alk-Ca^{2+}) = 50 mg/ℓ, i.e. Point 3.

Alkalinity, Ca^{2+} and pH at saturation (i.e. after dissolution of $CaCO_3$) are determined from the values for the respective lines through Point 3 i.e. saturation Alkalinity = 83 mg/ℓ, Ca^{2+} = 33 mg/ℓ and pH 8,55.

$CaCO_3$ dissolution potential = Alk(saturation) - Alk(initial)
= 83 - 80 = 3 mg/ℓ
= Ca^{2+}(saturation) - Ca^{2+}(initial)
= 33 - 30 = 3mg/ℓ

5.2.2 Stabilization solution procedures knowing the initial state

Assume the initial state of the water has been evaluated (as set out in Section 5.2.1) and it satisfies criteria (i), (iii), (iv) and (v) as listed in Section 5.1. Before the water can be discharged to the system it is required to satisfy criterion (ii), that is, it is necessary to condition the water to a precipitation potential of 4 mg/ℓ $CaCO_3$.

In practice the chemicals used to induce supersaturation, usually are lime, $Ca(OH)_2$ or soda ash, Na_2CO_3; to decrease supersaturation, usually carbon dioxide, CO_2. Dosage calculations to adjust the saturation state using the Modified Caldwell-Lawrence diagram usually must be carried out by successive approximation. The approach is summarized in the following steps:

(i) Establish the initial saturation state and Acidity of the water, see Section 5.2.1.

(ii) Assume an initial value for the mass concentration of selected dosing chemical to be applied.

(iii) Determine the changes in the stoichiometric parameters Alkalinity, Acidity and Ca^{2+} for the assumed mass of chemical dosage using Eqs (4.38 and 4.39).

(iv) Determine the new Alkalinity, Acidity and Ca^{2+} values for the changes determined in (iii) as, New value = orginal value + change due to dosing.

(v) Determine the new pH as follows: Plot the new Alkalinity, Acidity and Ca^{2+} values from (iv) in the Modified Caldwell-Lawrence diagram. The new aqueous phase equilibrium point is the point of intersection of the lines representing new Alkalinity and Acidity; new pH is the value of the pH line through the aqueous phase equilibrium point.

(vi) Assess the new saturation state as in (a) above. If supersaturation is still less than (or more than) the required value then increase (or decrease) the dosage assumed in (ii) and repeat steps (ii) to (iv). Usually only two or three iterations are required to obtain the required dosage.

EXAMPLE 3: Stabilization of an undersaturated water using $Ca(OH)_2$

Analysis of a water gives Alkalinity 180 mg/ℓ, Ca^{2+} 180 mg/ℓ (both as $CaCO_3$), pH 7,4, ionic strength 0,01 and temperature = 15°C. Determine the $Ca(OH)_2$ dosage required to adjust the saturation state to be supersaturated with 5 mg/ℓ $CaCO_3$ precipitation potential.

Solution

(i) Determine initial Acidity:

Plot in the Modified Caldwell-Lawrence diagram lines representing measured Alkalinity, pH and Ca^{2+} values. Following the procedure to determine the initial state set out in Example 2, the water has Acidity 218 mg/ℓ and is undersaturated by 15 mg/ℓ $CaCO_3$, see Fig 5.3(a).

(ii) Estimate $Ca(OH)_2$ dosage:

Assume $Ca(OH)_2$ dosage of, say, 10 mg/ℓ as $CaCO_3$.

(iii) Determine changes in stoichiometric parameters:

From Eqs (4.38 to 4.40) the changes in the stoichiometric parameters are

$$\text{Alkalinity (change)} = CO_3^{2-}\text{(added)} + HCO_3^-\text{(added)} + OH^-\text{(added)} - H^+\text{(added)}$$
$$= 0 + 0 + 10 - 0 = 10 \text{ mg/ℓ}$$

$$\text{Acidity (change)} = CO_2\text{(added)} + HCO_3^-\text{(added)} + H^+\text{(added)} - OH^-\text{(added)}$$
$$= 0 + 0 + 0 - 10 = -10 \text{ mg/ℓ}$$

$$Ca^{2+}\text{ (change)} = Ca^{2+}\text{(added)} = 10 \text{ mg/ℓ}.$$

(iv) Determine new values for the stoichiometric parameters:

New values for each of the mass parameters are determined from the original values plus the change due to dosing, i.e.

$$\text{Alkalinity (new)} = \text{Alkalinity(initial)} + \text{Alkalinity (change)}$$
$$= 180 + 10 = 190 \text{ mg/ℓ}$$

$$\text{Acidity (new)} = \text{Acidity(initial)} + \text{Acidity (change)}$$
$$= 218 - 10 = 208 \text{ mg/ℓ}$$

$$Ca^{2+}\text{ (new)} = Ca^{2+}\text{(initial)} + Ca^{2+}\text{ (change)}$$
$$= 180 + 10 = 190 \text{ mg/ℓ}.$$

(v) Determine pH after $Ca(OH)_2$ dosing:

The new aqueous phase equilibrium point in the diagram is given by the intersection point of the lines representing new Alkalinity (190 mg/ℓ) and new Acidity (208 mg/ℓ) i.e. Point 1 in Fig 5.3b. New pH is given by the value of pH line through the aqueous phase equilibrium point, i.e. pH 7,85.

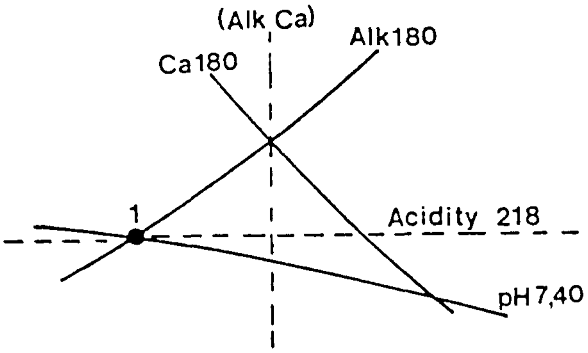


Fig 5.3a Example 3: Initial condition of water Alk 180 mg/ℓ, Ca^{2+} 180 mg/ℓ (both as $CaCO_3$), pH 7,4 (undersaturated).

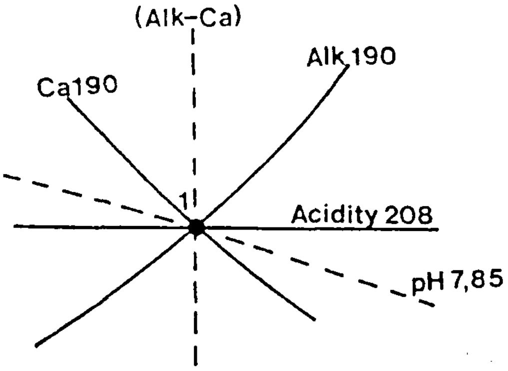


Fig 5.3b Example 3: Condition of water after addition of 10 mq/ℓ (as $CaCO_3$) of $Ca(OH)_2$. Water just saturated.

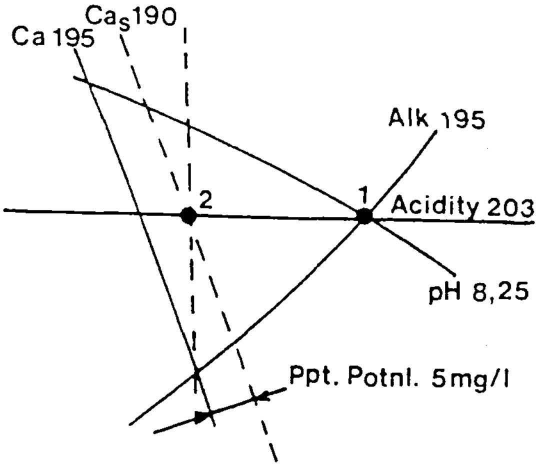


Fig 5.3c Example 3: Condition of water after addition of 15 mg/ℓ (as $CaCO_3$) of $Ca(OH)_2$. Supersaturated by 5 mg/ℓ $CaCO_3$.

(vi) Determine new precipitation potential:

Saturation state of the new condition (Alkalinity 190 mg/ℓ, Ca^{2+} 190mg/ℓ and pH 7,85) is determined as in (a) above giving a water just saturated with respect to $CaCO_3$, i.e. a dosage higher than 10 mg/ℓ $Ca(OH)_2$ (as $CaCO_3$) is required for supersaturation.

Assume $Ca(OH)_2$ dose of 15 mg/ℓ as $CaCO_3$ and repeat steps (ii) to (vi) giving the new condition Alkalinity 195 mg/ℓ, Acidity 203 mg/ℓ, Ca^{2+} 195 mg/ℓ, pH 8,25 and $CaCO_3$ precipitation potential of 5 mg/ℓ, see Fig 5.3(c).

EXAMPLE 4: Stabilization of an undersaturated water using Na_2CO_3.

Determine the Na_2CO_3 dosage required to adjust the saturation state of the raw water in Example 3 to supersaturation with a $CaCO_3$ precipitation potential of 5 mg/ℓ.

Solution

(i) Determine initial Acidity:

From the example above, the raw water has Acidity 218 mg/ℓ and is undersaturated with respect to $CaCO_3$ by 15 mg/ℓ.

(ii) Estimate Na_2CO_3 dosage:

Assume Na_2CO_3 dosage of, say, 20 mg/ℓ as $CaCO_3$.

(iii) Determine changes in stoichiometric parameters:

From Eqs (4.38 to 4.40) the changes in the stoichiometric parameters Alkalinity, Acidity and Ca^{2+} for the applied chemical dosage are

$$\begin{aligned}\text{Alkalinity (change)} &= CO_3^{2-}(\text{added}) + HCO_3^-(\text{added}) + OH(\text{added}) - H^+(\text{added})\\ &= 20 + 0 + 0 - 0 = 20 \text{ mg/ℓ as } CaCO_3\end{aligned}$$

$$\begin{aligned}\text{Acidity (change)} &= CO_2(\text{added}) + HCO_3^-(\text{added}) + H^+(\text{added}) - OH(\text{added})\\ &= 0 + 0 + 0 - 0 = 0\end{aligned}$$

$$\begin{aligned}Ca^{2+}\text{ (change)} &= Ca^{2+}(\text{added})\\ &= 0.\end{aligned}$$

(iv) Determine new values for the stoichiometric parameters:

New values for the mass parameters are determined from the initial values plus the changes, i.e.

$$\begin{aligned}\text{Alkalinity (new)} &= \text{Alkalinity(initial)} + \text{Alkalinity (change)}\\ &= 180 + 20 = 200 \text{ mg/ℓ}\end{aligned}$$

$$\begin{aligned}\text{Acidity (new)} &= \text{Acidity(initial)} + \text{Acidity (change)}\\ &= 218 + 0 = 218 \text{ mg/ℓ}\end{aligned}$$

Ca^{2+} (new) = Ca^{2+}(initial) + Ca^{2+} (change)
= 180 + 0 = 180 mg/ℓ.

(v) Estimate new pH:

The new aqueous phas equilibrium point in the MCL diagram is given by the intersection point of the lines representing new Alkalinity (200 mg/ℓ) and new Acidity (218 mg/ℓ). New pH is given by the value of the pH line through the new aqueous phase equilibrium point, i.e. pH 7,80 (not illustrated).

(vi) Estimate precipitation potential:

Saturation state of the new condition (Alkalinity 200 mg/ℓ, Ca^{2+} 180 mg/ℓ and pH 7,80) is determined as in (a) above as supersaturated with a precipitation potential of 5 mg/ℓ $CaCO_3$ (not illustrated).

EXAMPLE 5: Conditioning and Stabilization of Hartbeespoort dam water

Water from Hartbeespoort dam is to be treated for municipal distribution. Analysis of the raw water gives Ca^{2+} 108 mg/ℓ, Alkalinity 132 mg/ℓ (both as $CaCO_3$), pH(day) 9,6 and pH(night) 8,6, SO_4^{2-} 90 mg/ℓ, $C\ell^-$ 56 mg/ℓ, TDS 400 mg/ℓ and temperature of 20°C. Treatment of the water involves coagulation and flocculation using 50 mg/ℓ alum, $Al_2(SO_4)_3.14H_2O$, at pH 7,2. Adjustment of pH is with sulphuric acid. Determine or comment on the following:

(a) Estimate the sulphuric acid dosage to give a pH of 7,2 during coagulation and flocculation.

(b) Estimate the mass concentration of $Ca(OH)_2$ to adjust the water, prior to distribution, to have a precipitation potential of 5 mg/ℓ $CaCO_3$.

(c) Comment on the stability of the distribution water with regard to corrosiveness to cast iron pipes and fittings.

Solution

(a) Sulphuric acid dosage:

Comparing the day with the night time analyses, both have the same Alkalinity values but the pH during the day is significantly higher than that during the night. This would indicate that a net CO_2 abstraction (decreasing Acidity and increasing pH) takes place during daytime, and CO_2 injection (increasing Acidity and decreasing pH) at night. Such diurnal additions and abstractions of CO_2 are indicative of a high level of photosynthetic activity and biological respiration in an impoundment: During the daytime both photosynthesis (causing CO_2 abstraction) and plant (algal) respiration (causing CO_2 injection) take place simultaneously, however, the effects of photosynthesis dominate so that the net effect is one of CO_2 abstraction with associated pH increase. During the night only plant (algal) respiration takes place, causing CO_2 injection with associated pH decrease.

Summarizing the above, Alkalinity of the raw water remains constant, Acidity (and

C_T) increases at night and decreases during the day, concomitantly pH decreases at night and increases during the day.

For optimum coagulation the pH must be 7,2. The H_2SO_4 dose so that coagulation with 50 mg/ℓ alum can be carried out at pH 7,2 is found as follows: Taking the day time condition (pH 9,6) as an example:

(i) Deffeyes type diagram:

Select the Deffeyes type diagram from those listed in Appendix A with TDS 400 mg/ℓ and temperature of 20°C, see Fig 5.4.

(ii) Determine initial single phase equilibrium condition:

Draw in the diagram the lines representing initial pH and Alkalinity of the raw water (pH = 9,6 and Alkalinity = 132 mg/ℓ as $CaCO_3$). The lines intersect at Point 1. Acidity ordinate value of Point 1 gives initial Acidity = 88 mg/ℓ as $CaCO_3$.

(iii) Determine equilibrium condition after coagulation and flocculation:*

Plot in the diagram the line representing the required pH after coagulation and flocculation, i.e. pH = 7,2. The decrease in pH from 9,6 to 7,2 is effected by addition of strong acid (H_2SO_4) and alum. Precipitation of the aluminium salt as $Al(OH)_3$ causes abstraction of hydroxide, OH^-, species so that it also acts as a strong acid. From Eqs (4.38 and 4.39), the changes in Alkalinity and Acidity of the water (with all concentrations expressed in mg/ℓ as $CaCO_3$) are

$$\text{Alk(change)} = -\{H_2SO_4\text{(added)} + Al(OH)_3 \text{ precipitated}\}$$

$$\text{Acid(change)} = H_2SO_4\text{(added)} + Al(OH)_3 \text{ precipitated}$$

that is, the Alkalinity decreases and Acidity increases by the same amount. In the Deffeyes diagram this is represented by a line at 45° to the axes drawn from Point 1. When this line intersects the pH = 7,2 line establishes the final Alkalinity and Acidity during coagulation and flocculation, i.e. Point 2, giving Acidity(final) = 124 mg/ℓ as $CaCO_3$.

The difference in Acidity (or Alkalinity) between Points 1 and 2 gives the effective acid dose (i.e. H_2SO_4 dose plus $Al(OH)_3$ precipitated) i.e. Acidity change = Acidity(final) - Acidity(initial) = 124 - 88 = 36 mg/ℓ as $CaCO_3$.

(iv) Determine H_2SO_4 dosage:

The H_2SO_4 dosage is given by the difference between the total Acidity change (36 mg/ℓ) and that Acidity change due to $Al(OH)_3$ precipitation. Acidity change due to $Al(OH)_3$ precipitated is determined from the alum dosage (50 mg/ℓ) as follows:

Taking pH 9,6 as an example,

---

[*] For dosage conversions see Appendix C.

mmoles/ℓ alum added = mg/ℓ alum added/MW(alum)
= 50/594 = 0,084
mmol/ℓ $Al(OH)_3$ precipitated = 0,084
mmol/ℓ OH^- precipitated = 0,084.3
= 0,252
Acidity precipitated as $Al(OH)_3$ = 0,252.50
= 11,6 mg/ℓ as $CaCO_3$.
Thus, H_2SO_4 dosage required = Total Acidity change - Acidity change due to $Al(OH)_3$ precipitated
= 36 - 11,6 = 24,4 mg/ℓ as $CaCO_3$.

Applying the procedure above to this water, with initial Alkalinity constant at 132 mg/ℓ as $CaCO_3$, for a number of initial pH values between those for day and night (i.e. between pH 9,6 and 8,6), the Acidity changes required to adjust pH to 7,2 are listed in Table 5.1.

In column 6 of Table 5.1 are listed the required H_2SO_4 dosages for the range of initial pH values which, together with an alum dose of 50 mg/ℓ, give a final pH of 7,2. The H_2SO_4 dosage ranges from 24 mg/ℓ at pH 9,6 down to 8 mg/ℓ as $CaCO_3$ at pH 8,6.

The associated final Alkalinity values are given by the Alkalinity ordinate value of Point 2 in Fig 5.4 and are listed in column (5) of Table 5.1.

Table 5.1 Raw water Hartbeesport dam: H_2SO_4 dosage needed, in addition to 50 mg/ℓ Alum, to reduce pH from various initial values to pH 7,2. Initial Alkalinity = 132 mg/ℓ as $CaCO_3$.

pH initial	Acidity* initial	Acidity* final	Acidity* change	Alkalinity* final	H_2SO_4 dosage required*
9,6	88	124	36	96	25
9,4	101	130	29	103	18
9,2	110	134	24	108	13
9,0	117	138	21	111	10
8,8	121	141	20	112	9
8,6	126	145	19	113	8

* Concentration expressed in mg/ℓ as $CaCO_3$.

(b) $Ca(OH)_2$ dosage for a precipitation potential of 4 mg/ℓ $CaCO_3$:

After coagulation and flocculation at pH 7,2, the water is undersaturated with respect to $CaCO_3$ (irrespective of the initial pH and the concomitant mass concentration of H_2SO_4 added). It is required now to estimate the $Ca(OH)_2$ dosage to the water prior to distribution such that the water has a precipitation potential of 4 mg/ℓ $CaCO_3$. It would appear that the $Ca(OH)_2$ dosage to achieve this condition will vary depending on the initial pH of the water prior to coagulation and flocculation. As an example of $Ca(OH)_2$ dosage estimation, we will consider again the water which before coagulation and flocculation had a pH 9,6 (and Alkalinity 132 mg/ℓ and Ca^{2+} 108 mg/ℓ as $CaCO_3$).

After coagulation and flocculation the condition of the water is pH 7,2, Alkalinity 96 mg/ℓ, Ca^{2+} 108 mg/ℓ and Acidity 124 mg/ℓ (see Table 5.1). This condition establishes the initial state for the stabilization stage. $Ca(OH)_2$ dosage estimation is carried out in the following steps:

(i) Modified Caldwell-Lawrence diagram:

A Modified Caldwell-Lawrence (MCL) diagram is selected from the diagrams listed in Appendix B for TDS = 400 mg/ℓ (μ = 0,01) and temperature = 20°C, see Fig 5.5.

(ii) Plot initial state in MCL diagram:

In the diagram identify the lines representing Alkalinity 96 mg/ℓ, Ca^{2+} 108 mg/ℓ and Acidity 124 mg/ℓ. Note that the line representing pH 7,2 is not available in the plot so that the intersection point of Alkalinity and Acidity lines cannot be located. However, the initial acidity value (124mg/ℓ) was obtained from the Deffeyes diagram. Also the parameter Alk-Ca = -12 mg/ℓ can be plotted.

(iii) Estimate the initial saturation state:

Estimate the initial saturation state: The mass concentration of solid $CaCO_3$ which can either dissolve or precipitate is determined as follows: Draw in the lines representing (Alk-Ca) = 96 - 108 = -12 and Acidity = 124 mg/ℓ. If saturation is attained by dissolution or precipitation of $CaCO_3$, (Alk-Ca) and Acidity do not change from their initial values and the saturation value is given where these two intersect. The intersection point, Point 1, gives Alkalinity 118 mg/ℓ, Ca^{2+} = 130 mg/ℓ and pH 7,84. The mass of $CaCO_3$ that can dissolve or precipitate is given by the difference in Alkalinity (or Ca^{2+}) between the initial and saturated values. Taking the Alkalinity values,

$$\begin{aligned} CaCO_3 \text{ to be dissolved} &= \text{Alk(sat)} - \text{Alk(initial)} \\ &= 118 - 96 = 22 \text{ mg/}\ell. \end{aligned}$$

This water, then, has a dissolution potential of 22 mg/ℓ $CaCO_3$, that is, the water is very undersaturated and will be very aggressive to cement type materials - it needs to be adjusted to have the prescribed precipitation potential. This is achieved by adding $Ca(OH)_2$.

(iv) $Ca(OH)_2$ dosage

Estimation of $Ca(OH)_2$ dosage to adjust the water to have a $CaCO_3$ precipitation potential of 4 mg/ℓ $CaCO_3$ is carried out using the same procedure as set out in Example 3 above, i.e.

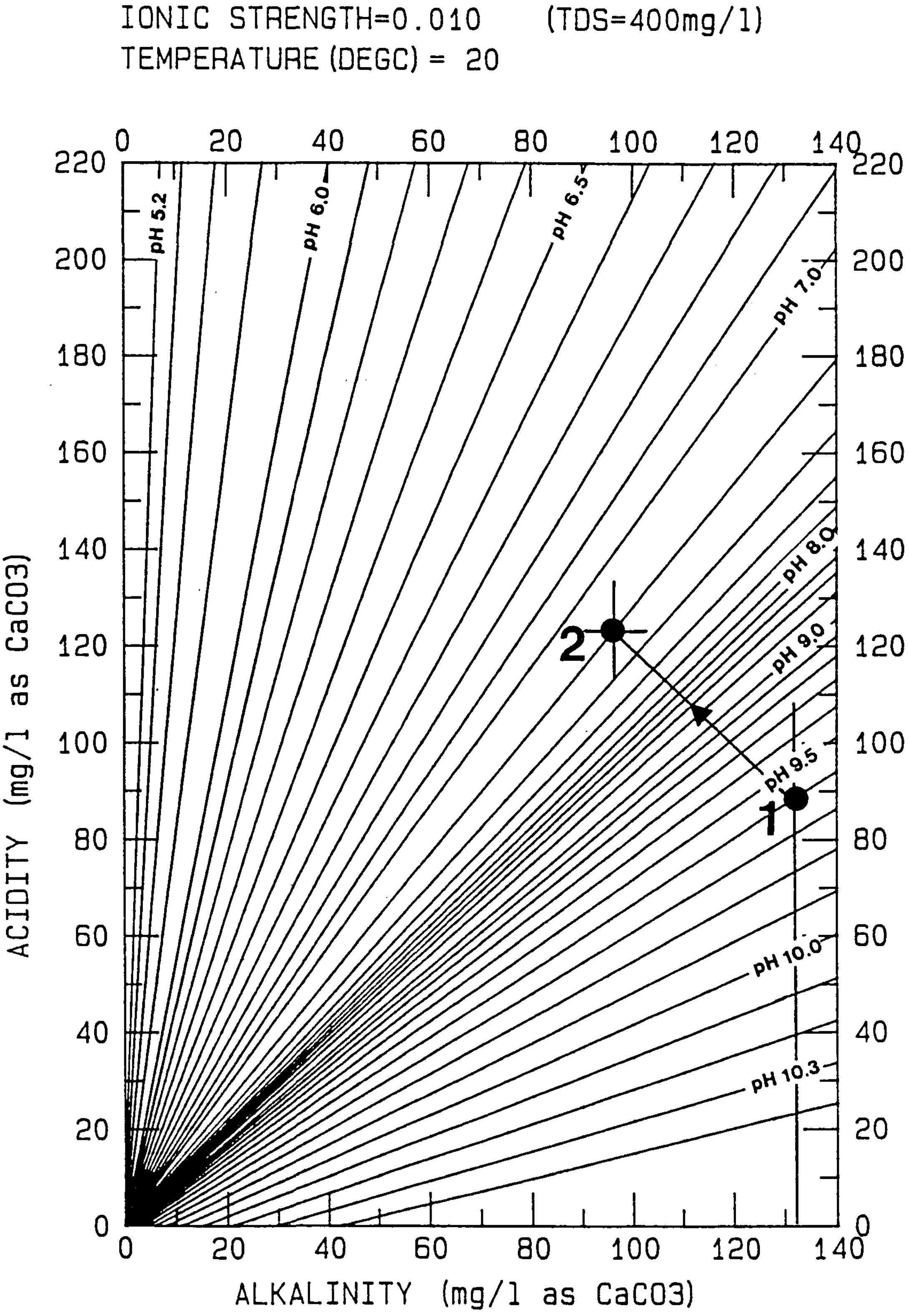


Fig 5.4 Example 5: Hartbeespoort dam water. Acidity and Alkalinity change to adjust water from pH 9,6 (Alkalinity 132 mg/ℓ) to pH 7,2 using strong acid.

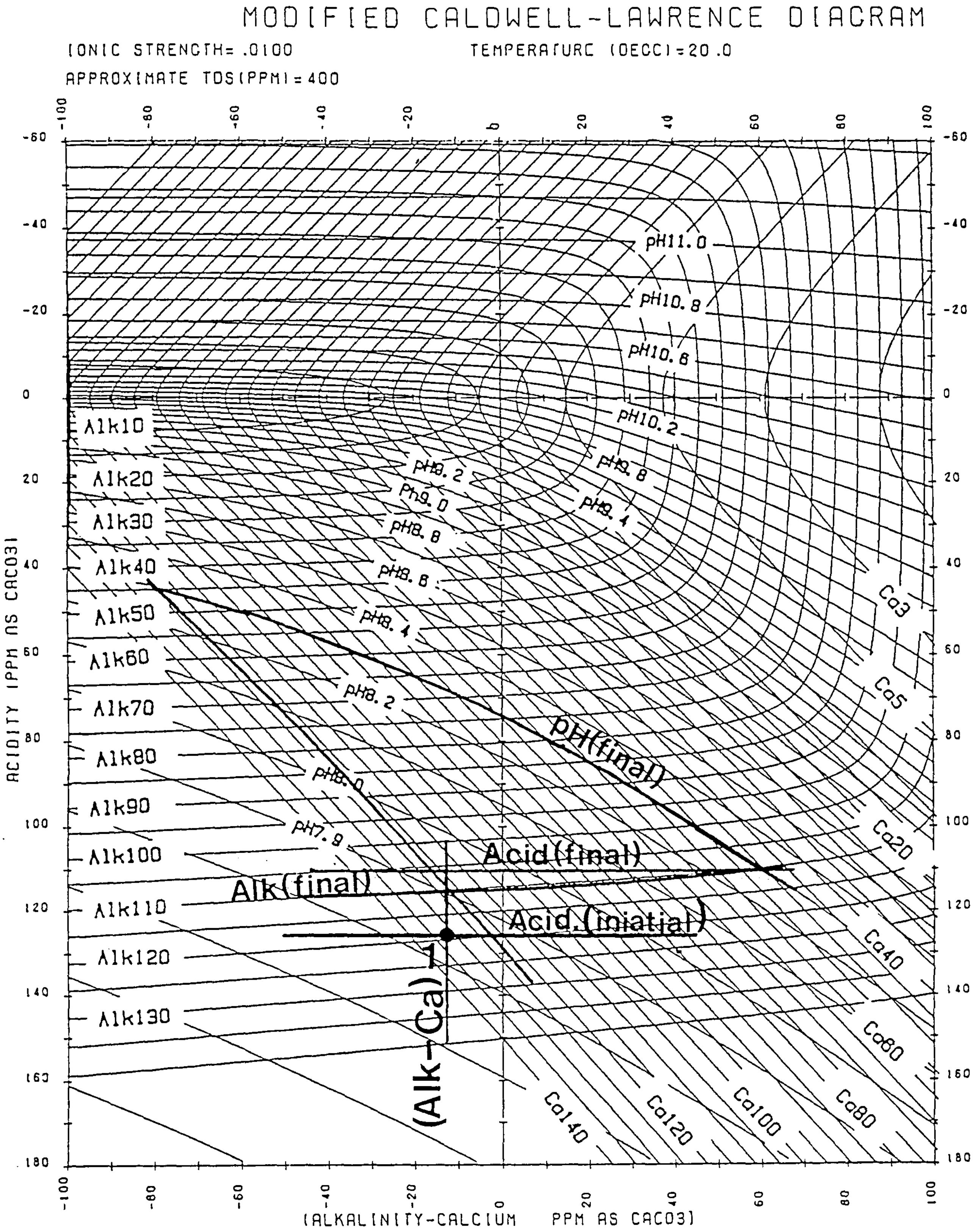


Fig 5.5 Example 5: Hartbeespoort dam water, 15 mg/ℓ $Ca(OH)_2$ is added to water with pH 7,2, Alkalinity 96 mg/ℓ, Acidity 124 mg/ℓ to give water with pH 8,3, Alkalinity 111 mg/ℓ and Ca^{2+} 123 mg/ℓ, and precipitation potential of 5 mg/ℓ $CaCO_3$.

Assume a $Ca(OH)_2$ dosage = 15 mg/ℓ as $CaCO_3$
From Eqs (4.38 and 4.39)

Alk(change) = 15 mg/ℓ
Acidity(change) = -15 mg/ℓ
Ca^{2+}(change) = 15 mg/ℓ
i.e.
Alk (new) = Alk(initial) + Alk(change)
= 96 + 15 = 111 mg/ℓ

Acid (new) = Acid(initial) + Acidity(change)
= 124 - 15 = 109 mg/ℓ

Ca^{2+} (new) = Ca^{2+}(initial) + Ca^{2+}(change)
= 108 + 15 = 123 mg/ℓ.

The new pH is given by the value of the pH line through the intersection point of lines for new Alk and new Acid, i.e. pH = 8,3.

(v) New saturation state and precipitation potential:

The new saturation state is determined as in (iii) above with (Alk-Ca) = (111-123) = -12 mg/ℓ and Acidity 109 mg/ℓ. The saturated Alk line, through the intersection point of these lines, is Alk(sat) = 106 mg/ℓ as $CaCO_3$; thus the $CaCO_3$ precipitation potential = Alk (new)- Alk(sat) = 111-106 = 5 mg/ℓ. Thus a $Ca(OH)_2$ dosage of 15 mg/ℓ as $CaCO_3$ is needed to give the water a $CaCO_3$ precipitation potential of 5mg/ℓ.

In Table 5.2 are listed the $Ca(OH)_2$ dosage with initial (raw water) pH necessary to give a precipitation potential of 5 mg/ℓ $CaCO_3$ to the flocculated water from Hartbeespoort dam (Table 5.1) calculated by the procedure outlined above.

(c) Corrosiveness of distribution water:

To evaluate the corrosiveness of the stabilized water, the water characteristics need to be judged against the guidelines in Section 5.1. The chemical characteristics satisfy all the criteria except guideline (iii), that the ratio $(C\ell^- + SO_4^{2-})$/Alkalinity $\lesssim$ 0,2, where species concentrations are expressed on the equivalent or the $CaCO_3$ equivalent scale.

Chloride content, $(C\ell^-)$ = 56 mg/ℓ
= 56.50/35 mg/ℓ as $CaCO_3$
= 80 mg/ℓ as $CaCO_3$

Sulphate content (SO_4^{2-}) = 90 mg/ℓ
= 90.50/48 mg/ℓ as $CaCO_3$
≈ 94 mg/ℓ as $CaCO_3$.

i.e. $(C\ell^- + SO_4^{2-})$ = (80+94) = 174 mg/ℓ as $CaCO_3$.

Thus an Alkalinity of 580 mg/ℓ is required to satisfy the requirement $(C\ell^{-}+SO_4^{2-})$/Alkalinity $\lesssim$ 0,2. Clearly it is not practical to adjust Alkalinity to this value and it must be accepted that the distribution water is likely to be corrosive to cast iron and mild steel - it would be advisable to use concrete, asbestos cement and/or plastic pipes, or lined metal pipes with inert plastics, resins or cement. Similarly, metal fittings should be lined with inert plastics or resins, or manufactured from special corrosion resistant metals.

Table 5.2: Hartbeespoort dam flocculated water: $Ca(OH)_2$ dosage for stabilization to give a precipitation potential of 5mg/ℓ $CaCO_3$. (For treatment prior to flocculation see Table 5.1).

Raw water pH	Flocculated Water, pH 7,2 Alk*	Acidity*	$Ca(OH)_2$ dosage*	Stabilized water pH	Alk(final)*	Ca*
9,6	96	124	15	8,3	111	123
9,4	103	130	14	8,25	117	122
9,0	111	138	14	8,2	125	122
8,6	113	145	15	8,2	128	123

* Concentration in mg/ℓ as $CaCO_3$.

EXAMPLE 6: Conditioning and stabilization in water reclamation

It is intended to reclaim a treated effluent having the following average characteristics: Ca^{2+} 70 mg/ℓ, Alkalinity 110 mg/ℓ (both as $CaCO_3$), pH 7,40, Cl^- 130 mg/ℓ (as Cl^-), SO_4^{2-} 70 mg/ℓ (as SO_4^{2-}), ionic strength 0,01 and temperature 20°C.

After coagulation and flocculation the water is required to have a turbidity level of less than 2,0 NTU. Laboratory tests have shown that the turbidity criterion can be satisfied by adding appropriate mass of $Fe_2(SO_4)_3$ at pH 6,0; over the range of influent water quality the dosages can range between 150 and 250 mg/ℓ (as $Fe_2(SO_4)_3$). The pH is controlled by $Ca(OH)_2$ addition. After settlement the supernatant is chlorinated with 15 mg/ℓ chlorine (as Cl_2). The water in the chlorination tank is maintained at pH 7,0 by dosing with $Ca(OH)_2$. The chlorinated flow is then filtered through a sand filter and passed through an activated carbon column. Thereafter the water is stabilized to calcium carbonate saturation. It is required to determine

(a) $Ca(OH)_2$ dosages to the flocculation tank to maintain a pH = 6,0 for ferric sulphate dosages of 150 mg/ℓ, 200 mg/ℓ and 250 mg/ℓ (as $Fe_2(SO_4)_3$).

(b) $Ca(OH)_2$ dosage to the chlorination tank to maintain a pH = 7,0 with a chlorine dosage of 15 mg/ℓ (as Cl_2).

(c) Calcium carbonate saturation state after chlorination.

(d) $Ca(OH)_2$ dosage to the stabilization tank to adjust the effluent water to a state of saturation with respect to calcium carbonate.

Solution

(a) $Ca(OH)_2$ dosage in the flocculation unit:

For optimum coagulation the pH must be 6,0. The $Ca(OH)_2$ dose, so that coagulation with ferric sulphate can be carried out at pH 6,0, is found as follows: Taking the ferric sulphate dosage of 200 mg/ℓ (as $Fe_2(SO_4)_3$) as an example:

(i) Deffeyes type diagram:

Select the Deffeyes type diagram from those listed in Appendix A with TDS 400 mg/ℓ (μ = 0,01) and temperature of 20°C, see Fig 5.6.

(ii) Determine initial single phase equilibrium state:

Draw in the diagram the lines representing initial pH and Alkalinity of the raw water (pH = 7,4 and Alkalinity = 110 mg/ℓ as $CaCO_3$). The lines intersect at Point 1. Acidity ordinate value of Point 1 gives initial Acidity = 130 mg/ℓ as $CaCO_3$.

(iii) Determine equilibrium state after coagulation and flocculation:

Plot in the diagram the line representing the required pH after coagulation and flocculation, i.e. pH = 6,0. The required change in pH from 7,4 to 6,0 is effected by addition of ferric sulphate and $Ca(OH)_2$. Precipitation of the ferric salt as $Fe(OH)_3$ causes abstraction of OH^- so that it acts as a strong acid; the required ferric sulphate dosage reduces pH to well below pH = 6,0 so that OH^- must be added simultaneously, by $Ca(OH)_2$ addition, to obtain the desired pH. From Eqs (4.38 and 4.39), the changes in Alkalinity and Acidity of the water (with all concentrations expressed in mg/ℓ as $CaCO_3$) are

Alk(change) = $Ca(OH)_2$ (added) - $Fe(OH)_3$ (precipitated)
Acid(change) = $-Ca(OH)_2$ (added) + $Fe(OH)_3$ (precipitated).

That is, the Alkalinity and Acidity changes are equal but opposite. In the Deffeyes diagram, a simultaneous Alkalinity decrease and Acidity increase of equal magnitude, is represented by a line at 45° to the axes drawn from Point 1. Where this line intersects the pH = 6,0 line establishes the final Alkalinity and Acidity during coagulation and flocculation, i.e. Point 2, giving Alkalinity(final) = 38 mg/ℓ and Acidity(final) = 202 mg/ℓ (both as $CaCO_3$).

The difference in acidity gives the net or effective acid addition due to $Fe(OH)_3$ precipitation and $Ca(OH)_2$ addition, i.e.

Acidity(change) = Acidity(final) - Acidity(initial)

= 202 - 130 = 72 mg/ℓ as $CaCO_3$

(iv) Determine $Ca(OH)_2$ dosage:

The $Ca(OH)_2$ dosage is given by the difference between the net Acidity change (72 mg/ℓ) and that Acidity change due to $Fe(OH)_3$ precipitation. Acidity change due to $Fe(OH)_3$ precipitation is determined from the ferric sulphate dosage (200 mg/ℓ) as follows:

m.mol/ℓ $Fe_2(SO_4)_3$ = mg/ℓ ferric sulphate added/
MW (ferric sulphate)
= 200/394 = 0,508
m.mol/ℓ $Fe(OH)_3$ precipitated = 0,508.2
= 1,016
m.mol/ℓ OH^- precipitated = 1,016.3
= 3,048

Acidity increase due to $Fe(OH)_3$ precipitation = 3,048.50
= 152,4 mg/ℓ as $CaCO_3$

Now, net Acidity change equals change due to $Fe(OH)_3$ precipitation minus $Ca(OH)_2$ dosage, thus

$Ca(OH)_2$ dosage = Acidity change due to $Fe(OH)_3$ precipitation - total acidity change
= 152,4-72 = 80,4 mg/ℓ as $CaCO_3$.

Repeating the procedure above for the same water but for a number of ferric sulphate dosages, between 150 and 250 mg/ℓ, the $Ca(OH)_2$ dosages required to adjust pH to 6,0 are listed in Table 5.3. The associated final Alkalinity, Acidity and calcium values (determined from the initial Ca^{2+} concentration plus the mass concentration of $Ca(OH)_2$ added expressed as $CaCO_3$) are also listed.

(b) $Ca(OH)_2$ dosage in the chlorination unit: After coagulation and flocculation at pH 6,0, the water is chlorinated with 15 mg/ℓ $C\ell_2$. It is now necessary to estimate the $Ca(OH)_2$ dosage to maintain the pH in the chlorination tank at pH 7,0. As an example of $Ca(OH)_2$ dosage estimation, we will consider again the water dosed with 200 mg/ℓ ferric sulphate in the coagulation/flocculation phase.

After coagulation and flocculation the condition of the water is pH 6,0, Alkalinity 38 mg/ℓ, Ca^{2+} 150 mg/ℓ and Acidity 202 mg/ℓ (see Table 5.3). This condition establishes the initial state for the chlorination stage. $Ca(OH)_2$ dosage estimation is carried out in the following steps:

(i) Determine equilibrium state after chlorination

Plot in Fig 5.6 the line representing the required pH after (and during) chlorination, i.e. pH = 7,0. The change in pH from 6,0 to 7,0 is effected by addition of $C\ell_2$ and

Table 5.3 $Ca(OH)_2$ dosage for coagulation at pH 6,0 with ferric sulphate dosages of 150 to 250 mg/ℓ for water with Ca^{2+} 70 mg/ℓ, Alkalinity 110mg/ℓ (both as $CaCO_3$) and pH 7,4.

Ferric sulphate dosage (mg/ℓ)	$Ca(OH)_2$ dosage	Ca^{2+}	Alkalinity	pH
	mg/ℓ as $CaCO_3$			
150	42,2	112,2	38	6,0
200	80,4	150,4	38	6,0
250	118,4	178,4	38	6,0

$Ca(OH)_2$. Addition of Cl_2 increases Acidity and decreases Alkalinity (without changing C_T) so that it acts as a strong acid and will depress pH below the initial value of pH 6,0. Consequently, $Ca(OH)_2$ must be added simultaneously to obtain the required pH = 7,0. From Eqs (4.38 and 4.39), the changes in Alkalinity and Acidity of the water (with all concentrations expressed in mg/ℓ as $CaCO_3$) are

Alk(change) = $Ca(OH)_2$ (added) - Cl_2 (added)
Acid(change) = -$Ca(OH)_2$ (added) + Cl_2 (added)

That is, Alkalinity and Acidity changes are equal but opposite. In the Deffeyes diagram this is represented by a line at 45° to the axes drawn from Point 2. Where this line intersects the pH 7,0 line establishes the final Alkalinity and Acidity during chlorination, i.e. Point 3 giving Alkalinity(final) = 98 mg/ℓ and Acidity = 142 mg/ℓ (both as $CaCO_3$).

The increase in Alkalinity gives the effective strong base dose (i.e. $Ca(OH)_2$ dosage minus chlorine dosage), i.e.

Alk(increase) = Alk(final) - Alk(initial)
= 98 - 38 = 60 mg/ℓ as $CaCO_3$

(ii) Determine $Ca(OH)_2$ dosage:

The $Ca(OH)_2$ dosage is given by the sum of the Alkalinity increase between Points 2 and 3 (i.e. 60 mg/ℓ) plus the Alkalinity removed due to $Cℓ_2$ addition. Alkalinity removed due to chlorination is determined from the chlorine dosage (15 mg/ℓ as Cl_2) as follows:

m.mol/ℓ Cl_2 added = mg/ℓ Cl_2 added/MW of Cl_2
= 15/70 = 0,214
Alkalinity decrease due to Cl_2 addition = 0,214.2.50
= 21,4 mg/ℓ as $CaCO_3$
Thus $Ca(OH)_2$ dosage = Alk(increase) + Alk (decrease) due to Cl_2 addition
= 60 + 21,4 = 81,4 mg/ℓ as $CaCO_3$.

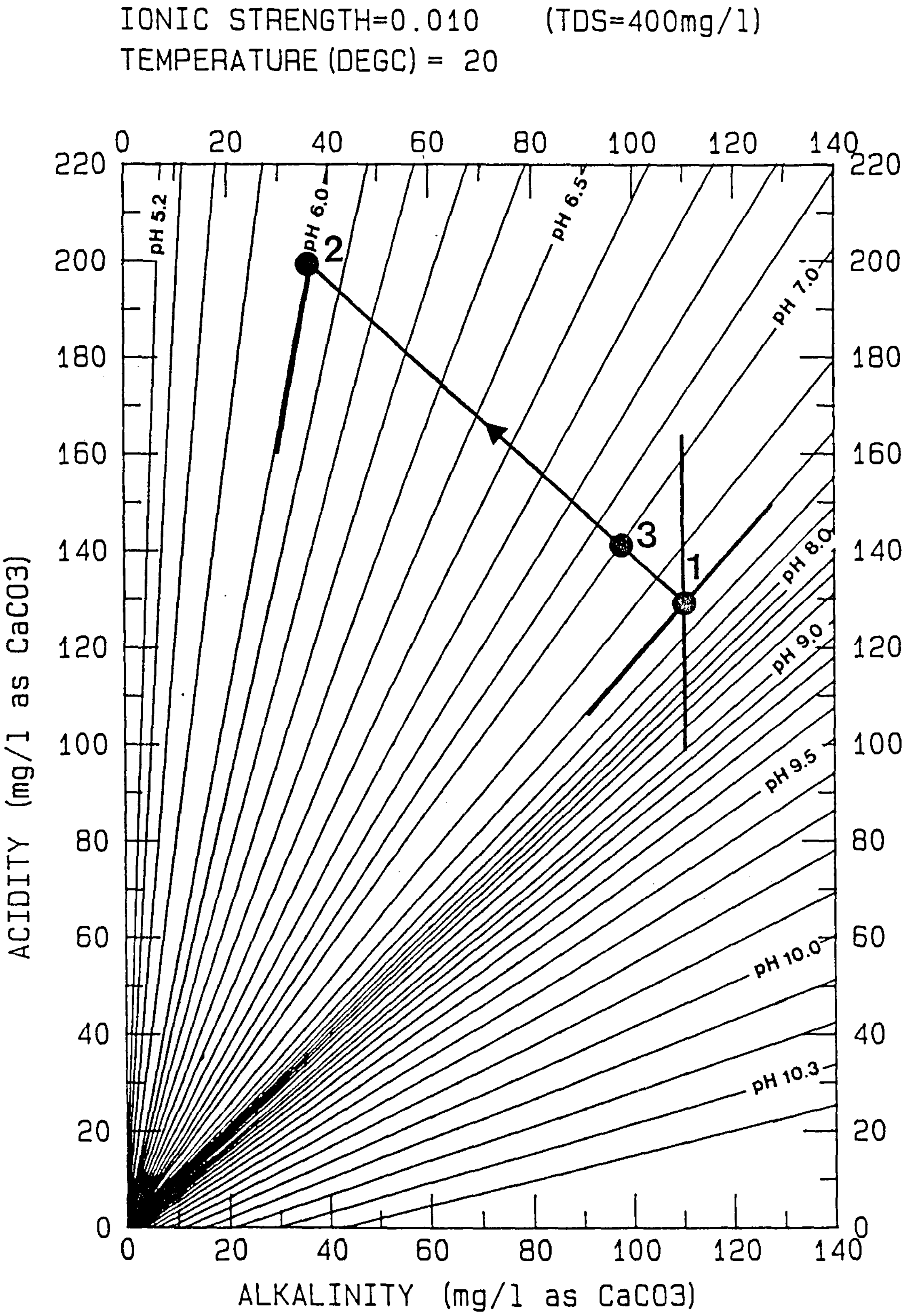


Fig 5.6 Example 6: Addition of $Ca(OH)_2$ to water with pH 7,4 and Alkalinity 110 mg/ℓ as $CaCO_3$.

Note that this $Ca(OH)_2$ dosage depends only on the Alkalinity and Acidity (or pH) of the water entering the chlorination unit, the chlorine dosage applied and the pH required in the chlorination process. Consequently, in this example, because the Alkalinity and pH after coagulation have fixed values, *independent of the ferric sulphate dosage applied* (see Table 5.4), the $Ca(OH)_2$ dosage to maintain pH = 7,0 during chlorination has a fixed value of 81,4 mg/ℓ.

(c) Calcium carbonate saturation state after chlorination: After chlorination the condition of the water is pH = 7,0, Alkalinity 98 mg/ℓ and Acidity 142 mg/ℓ (both as $CaCO_3$); the calcium concentration depends on the ferric sulphate dosage applied for coagulation and equals the influent Ca^{2+} value plus the sum of the $Ca(OH)_2$ dosages applied (as $CaCO_3$) for coagulation and disinfection processes (see Table 5.4).

Assessment of the calcium carbonate saturation state is carried out in a MCL diagram for µ 0,01 and temperature 20°C following the procedure set out in Example 2 of this chapter. For each of the three ferric sulphate dosages considered, the water is undersaturated with respect to calcium carbonate after chlorination (see Table 5.4).

(d) $Ca(OH)_2$ dosage to adjust effluent to saturation with respect to calcium carbonate. After chlorination at pH 7,0, the water is undersaturated with respect to $CaCO_3$ (irrespective of the ferric sulphate dosage applied for coagulation at pH 6,0). It is required now to estimate the $Ca(OH)_2$ dosage to the water prior to distribution such that the water is just saturated with respect to $CaCO_3$. As an example of $Ca(OH)_2$ dosage estimation, we will consider again the water which required 200 mg/ℓ ferric sulphate for the coagulation process.

After chlorination the condition of the water is pH 7,0, Alkalinity 98 mg/ℓ, Acidity 142 mg/ℓ and Ca^{2+} 231 mg/ℓ (all as $CaCO_3$). Estimation of $Ca(OH)_2$ dosage to adjust the water to saturation with respect to $CaCO_3$ is carried out using the same procedure as set out in Example 3 of this chapter, i.e.

Table 5.4 $Ca(OH)_2$ dosage and condition of water after chlorination with 15 mg/ℓ Cl_2 at pH 7,0.

Ferric sulphate dosage mg/ℓ	$Ca(OH)_2$ dosage	Ca^{2+}	Alkalinity	Acidity	pH	$CaCO_3$ dissolution potential (mg/ℓ)
			mg/ℓ as $CaCO_3$			
150	81,4	193	98	142	7,0	32
200	81,4	231	98	142	7,0	29
250	81,4	269	98	142	7,0	28

(i) Modified Caldwell-Lawrence diagram:

A Modified Caldwell-Lawrence diagram is selected from the diagrams listed in Appendix B for μ = 0,01 and temperature 20°C.

(ii) $Ca(OH)_2$ dosage:

Assume a $Ca(OH)_2$ dosage = 17 mg/ℓ as $CaCO_3$
From Eqs (4.38 and 4.39)
Alk(change) = 17 mg/ℓ
Acidity(change) = -17 mg/ℓ
Ca^{2+}(change) = 17 mg/ℓ
i.e.
Alk (new) = Alk(initial) + Alk(change)
= 98 + 17 = 115 mg/ℓ
Acid (new) = Acid(initial) + Acidity(change)
= 142 - 17 = 125 mg/ℓ
Ca^{2+} (new) = Ca^{2+}(initial) + Ca^{2+}(change)
= 231 + 17 = 248 mg/ℓ.

The new pH is given by the value of the pH line through the intersection point of lines for new Alk and new Acidity, i.e. pH 7,60.

(iii) New saturation state and precipitation potential

The new saturation state is determined as in Example 5(b)(iii) above with (Alk-Ca^{2+}) = (115-248) = -133 mg/ℓ and Acidity 125 mg/ℓ. The saturated Alkalinity line through the intersection point of these lines is Alk(sat) = 116 mg/ℓ which equals the Alkalinity value for the assumed $Ca(OH)_2$ dosage of 17 mg/ℓ. Thus, after $Ca(OH)_2$ dosing of 17 mg/ℓ the water is just saturated with respect to $CaCO_3$. The $Ca(OH)_2$ dosage for stabilization, and the associated characteristics of the effluent water, for the various ferric sulphate dosages applied in coagulation are listed in Table 5.5.

Table 5.5 $Ca(OH)_2$ dosage required for stabilization to saturation with respect to $CaCO_3$ for various ferric sulphate dosages used in the coagulation unit.

Ferric sulphate dosage (mg/ℓ)	$Ca(OH)_2$ dosage	Ca^{2+}	Alk	pH
		mg/ℓ as $CaCO_3$		
150	20	213	118	7,63
200	17	248	115	7,60
250	15	284	113	7,54

The calculations in the examples above assumed pure $Ca(OH)_2$. In commercial lime the $Ca(OH)_2$ content may range from 60-70 percent and the calcium concentration per unit of

$Ca(OH)_2$ may differ from that in pure $Ca(OH)_2$. Consequently if commercial lime is used the alkalinity additions per unit mass of $Ca(OH)_2$ need to be known, so also the calcium value, and it may be necessary to repeat the calculations above to determine the commercial lime dosages.

5.3 STABILIZATION OF CALCIUM AND CARBONATE SPECIES DEFICIENT WATERS

Calcium and carbonate species deficient waters are identified by having low calcium and Alkalinity values (usually both less than about 20 mg/ℓ as $CaCO_3$) and low pH (pH $\leqslant$ 6). In South Africa calcium and carbonate species deficiencies are found in waters derived from the Table Mountain sandstone regions on the eastern and southern seaboards. These waters naturally occur as surface waters in many parts of the world. A typical example is the natural water feeding Kloof Nek treatment plant, Cape Town, which, after colour removal, has $Ca^{2+} \approx 1$ mg/ℓ, Alkalinity ≈ 0 mg/ℓ (both as $CaCO_3$) and pH $\approx 4,8$.

Stabilization of calcium and carbonate species deficient waters requires increasing both Ca^{2+} and Alkalinity concentrations to values satisfying the minimum criteria to control corrosion and aggression, i.e. increasing both to $>$ 50 mg/ℓ as $CaCO_3$, and adjusting pH so that the final water has pH in the range $6,5 < pH < 9,5$ and is supersaturated by about 4 mg/ℓ as $CaCO_3$ (see Section 5.1). Chemical conditioning to achieve these criteria involves addition of $Ca(OH)_2$ for Ca^{2+} and Alkalinity adjustment, and addition of CO_2 for pH adjustment.

5.3.1 Characterization of calcium and carbonate species deficient waters

The first step in resolving a conditioning problem is to determine the relevant characteristics of the water to be conditioned, via measurement of the parameters listed in (a) to (d) in Section 5.1. However, for carbonate species deficient waters accurate measurement of Alkalinity and pH (to characterize the carbonate system) are not straightforward for the following reasons:

(i) Alkalinity of these waters is very low, often less than about 5 mg/ℓ as $CaCO_3$. An error in the Alkalinity determination by titration to an incorrect pH endpoint due to the misapplication of colorimetric methods, or an error in the pH reading, or wrong choice of endpoint pH, can give rise to an error of up to four hundred percent in the Alkalinity value; this in turn gives rise to errors of the same magnitude in the calculated value for Acidity. The magnitude of the error is illustrated in Table 5.6, where the Acidity error is listed for an error in the Alkalinity determination for a carbonate species deficient water with true Alkalinity 1 mg/ℓ as $CaCO_3$ and pH 5,6. Clearly, if Alkalinity is to be used to characterize the raw water an extremely accurate method of measurement is required. The normal procedures are inadequate; a method, which gives accurate values, is the Gran titration technique, as set out in Appendix D.

(ii) Accurate measurement of pH in carbonate species deficient waters is difficult due to the extremely low buffer capacity of these waters. Unless appropriate procedures are adopted it is possible to obtain measurement errors of up to one pH unit with associated high errors in the Alkalinity determination and calculated Acidity. Table

5.7 lists the error in the calculated Acidity value due to error in pH measurement for water with true pH 5,6 and true Alkalinity 1 mg/ℓ as $CaCO_3$. In low Alkalinity water if pH is used to determine Acidity, the measurement should be to within 0,1 pH units of the true value.

Table 5.6 Error in calculated Acidity due to an error in Alkalinity measurement for water with pH 5,6 and Alkalinity 1 mg/ℓ as $CaCO_3$.

Alkalinity error mg/ℓ at $CaCO_3$	Acidity error mg/ℓ as $CaCO_3$
1	15
2	30
3	45
4	60

Table 5.7 Error in calculated Acidity value due to error in pH measurement for water with true pH 5,6 and Alkalinity 1 mg/ℓ.

pH error	Acidity error (mg/ℓ as $CaCO_3$)
+ 0,4	5
+ 0,2	4
- 0,2	6
- 0,4	16
- 0,6	40

To ensure such accuracy the precautions for pH measurement set out in Section 5.3.2 must be observed.

5.3.2 Suggested procedures for pH and Alkalinity measurements

(a) pH measurement: Because of the extremely low buffering capacity of these waters, the following procedure should be adopted in making pH measurements:

(i) Standardize the probe against National Bureau of Standards (NBS) buffers.

(ii) Rinse the glass and reference probes thoroughly with distilled water.

(iii) Probes must be dipped into at least three separate 200 mℓ samples of the water to be analyzed and kept in each sample for about 30 seconds with gentle stirring of the sample. This adapts the probe to the low carbonate species low buffering capacity water, and the liquid junction effect is stabilized.

(iv) Probes must be inserted into the test solution, and the solution gently stirred for at least three minutes before taking the reading - in low buffered waters the response of the electrode system is slow.

(b) Alkalinity measurement: Alkalinity is measured using a Gran titration as set out in Appendix D. Before carrying out the titration the probes should be standardized and rinsed as set out for pH measurement in (a) above.

(c) HCO_3^- acidity measurement: To avoid gross errors in characterizing carbonate species deficient waters it is advisable that not only Alkalinity and pH measurements be carried out, but HCO_3^- acidity also, as a check. HCO_3^- acidity is measured by titrating a water sample to the bicarbonate equivalence point (Phenolphthalein colorimetric endpoint) with standard base or carbonate. For carbonate species deficient waters (with pH ≈ 5,5) this measurement is more easily carried out than the Total Alkalinity titration for the following reason: The endpoint to the HCO_3^- acidity titration (the bicarbonate equivalence point) is independent of the total carbonate species concentration and minimally affected by ionic strength and temperature. Consequently, titration to the Phenolphthalein colorimetric endpoint results in insignificant titration errors. That is, a Gran titration is not essential for this measurement. Either a pH endpoint or colorimetric endpoint can be used. The colorimetric endpoint is sharp and quite satisfactory; the pH endpoint can be identified easily from the corresponding inflection point in the titration curve. However, in Alkalinity determination using the Gran method pH observations above and below the $H_2CO_3^*$ equivalence points usually are made so that data for the Gran method to determine HCO_3^- acidity also is available (see Appendix D).

EXAMPLE 7: Characterization of calcium and carbonate species deficient water.

Measurement on a calcium cabonate species deficient water (after colour removal) gives pH 6,0 and Ca^{2+} 5 mg/ℓ as $CaCO_3$. Temperature at time of test, 20°C. Total inorganic dissolved solids, 40 mg/ℓ. HCO_3^- acidity is measured by titrating a 100 mℓ sample with 0,01 M standard strong base to the Phenolphthalein endpoint; volume of base titrated, 0,90 mℓ.

Alkalinity is measured by means of a Gran titration on a 100 mℓ sample with 0,020 M standard strong acid. The titration values are listed in Table 5.8. Determine the characteristics of the carbonate system in the water.

(a) Alkalinity determination: In Appendix D is set out the development of Gran functions for determining the various forms of alkalinity and acidity. The Gran function, F_1, for determining Alkalinity is

$$F_{1x} = 10^{-pH_x} (V_I + v_x) = 10^{-pH_x} (V_{Tx}) \qquad (5.\ 1)$$

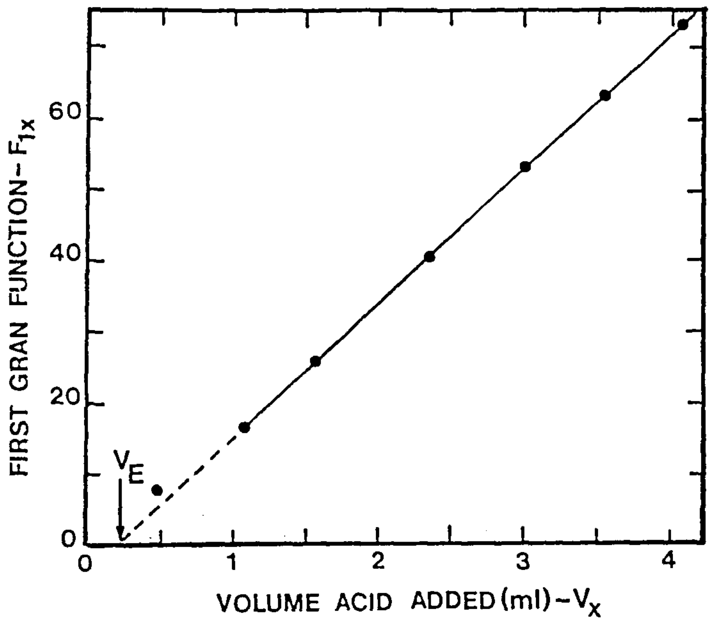


Fig 5.7 Example 7: Alkalinity determination on a low Alkalinity water using a Gran function. Extrapolation of plot of Gran function F_{1x} versus v_x to intersect v_x axis gives acid titrant for Alkalinity measurement, v_E = 0,20, mℓ.

where V_I = initial volume of sample in mℓ.

v_x = volume of strong acid added at any point in the titration in mℓ.

V_{Tx} = total volume made up of initial volume plus volume of titrant added

pH_x = pH value after addition of v_x mℓ of strong acid.

In the region pH $\lesssim$ 3,8 a plot of F_{1x}, determined from observed values for pH_x and v_x, versus v_x is linear, and extrapolation to F_{1x} = 0 gives the volume of strong acid required to titrate the water to the carbonic acid equivalence point.

In Table 5.8 are listed observed pH values, pH_x, against volume of standard strong acid added, v_x, and the corresponding value for the Gran function F_{1x} determined from Eq (5.1). In Figure 5.7 is a plot of v_x versus F_{1x} from data listed in Table 5.8. Extrapolation

Table 5.8 Gran titration results for measuring Alkalinity of a calcium carbonate species deficient water. Sample volume = 100 mℓ and standard acid 0,020 M.

pH_x	v_x mℓ	V_{Tx} mℓ	F_{1x}
3,80	1,05	101,05	0,0160
3,60	1,55	101,55	0,0255
3,40	2,35	102,35	0,0407
3,16	4,15	104,15	0,0721

of the linear plot to $F_{1(x)} = 0$ gives volume of standard acid to titrate the sample to the $H_2CO_3^*$ equivalence point, v_E, as 0,2 mℓ. From Appendix D,

$$\text{Alkalinity} = \frac{\bar{C}_a \cdot v_E}{V_I} \cdot 5.10^4$$

$$= \frac{0,02 \cdot 0,2}{100} \cdot 50.10^4$$

$$= 2 \text{ mg/ℓ as } CaCO_3$$

where $\bar{C}_a$ = molarity of standard acid
v_E = volume of standard acid to titrate the sample to the $H_2CO_3^*$ equivalence point (mℓ).

(b) HCO_3^- acidity measurement:

$$HCO_3^- \text{ acidity} = \bar{C}_b.(v_e/V_I).5.10^4$$
$$= 0,01.(0,9/100).5.10^4$$
$$= 4,5 \text{ mg/ℓ as } CaCO_3$$

where $\bar{C}_b$ = molarity of standard base
v_e = volume of standard base to titrate the sample to the Phenolpthalein endpoint.
V_I = sample volume.

(c) Determination of Acidity: Acidity of the water can be determined from any pair of the three measurements, i.e. from HCO_3^- acidity and Alkalinity, pH and Alkalinity, and pH and HCO_3^- acidity. Any two of the three determinations should give closely the same value provided no serious measurement error has been made.

(i) From HCO_3^- acidity and Alkalinity: From Eq (4.24)

$$\text{Acidity} = 2.HCO_3^- \text{ acidity} + \text{Alkalinity}$$
$$= 2.4,5 + 2,0$$
$$= 11,0 \text{ mg/ℓ as } CaCO_3.$$

(ii) From pH and Alkalinity: Select the Deffeyes type diagram for the ionic strength and temperature of the raw water, Fig 5.8. Select, or draw in the line representing pH 6,0 and draw in the line representing Alkalinity = 2 mg/ℓ as $CaCO_3$. Intersection is at Point 1. Read off the Acidity value of Point 1 on the Acidity ordinate,

Acidity = 11 mg/ℓ as $CaCO_3$

Agreement in Acidity between (i) and (ii) above indicates that there is no serious measurement error inherent in pH, Alkalinity and HCO_3^- acidity measurements on the raw water.

5.3.3 Solution procedure for stabilizing calcium and carbonate species deficient water.

Calculations for determining $Ca(OH)_2$ and carbon dioxide dosages to stabilize calcium and carbonate species deficient waters are carried out with the aid of a MCL diagram and Deffeyes type diagram in the following steps (It is assumed that Alkalinity and pH of the water to be treated, Alk(initial) and pH(initial), have been determined as set out in Section 5.3.2 above):

(i) Select the appropriate Deffeyes and MCL diagrams for the ionic strength and temperature of the water from those listed in Appendices A and B, respectively.

(ii) Determine the initial Acidity, Acid(initial). On the Deffeyes diagram find the intersection of lines representing Alk(initial) and pH(initial) to give Acid(initial).

(iii) Determine $Ca(OH)_2$ dosage (in mg/ℓ as $CaCO_3$) to adjust both Alkalinity and Ca^{2+} values to at least 50 mg/ℓ (as $CaCO_3$) using Eqs (4.38 and 4.39) as follows:

If Alk(initial) is less than initial Ca^{2+}:

$$Ca(OH)_2 \text{ dosage} = \text{Alk(final)} - \text{Alk(initial)} \quad (5.\ 2)$$

Alternatively, if Alk(initial) is greater than initial Ca^{2+}:

$$Ca(OH)_2 \text{ dosage} = Ca^{2+}\text{(final)} - Ca^{2+}\text{(initial)} \quad (5.\ 3)$$

(iv) Determine the CO_2 dosage to give a pH(final) such that the water will be supersaturated with a precipitation potential of 4 mg/ℓ $CaCO_3$. The crux of this determination is to find the final Acidity of the water when it leaves the works, i.e. Acid(final). It is found readily by noting that during precipitation of $CaCO_3$ the Acidity does not change (Eq 4.39). Hence, if one could determine the saturated values for Alkalinity and Ca^{2+}, then the Acidity(sat) can be determined in the MCL diagram, and, this value equals the required Acidity of the water when it leaves the works.

Alkalinity at saturation, Alk(sat):

$$\begin{aligned}\text{Alk(sat)} &= \text{Alk(final)} - \text{Alk. loss due to precipitation of 4 mg/ℓ } CaCO_3 \\ &= \text{Alk(final)} - 4\end{aligned}$$

Acidity at saturation, Acid(sat):

During $CaCO_3$ precipitation the Acidity does not change. Hence

Acid(sat) = Acid(final)

Now the Acid(sat) value can be read off the MCL diagram because its value is given by the Acidity ordinate value of the intersection of Alk(sat) and Ca^{2+}(sat) lines.

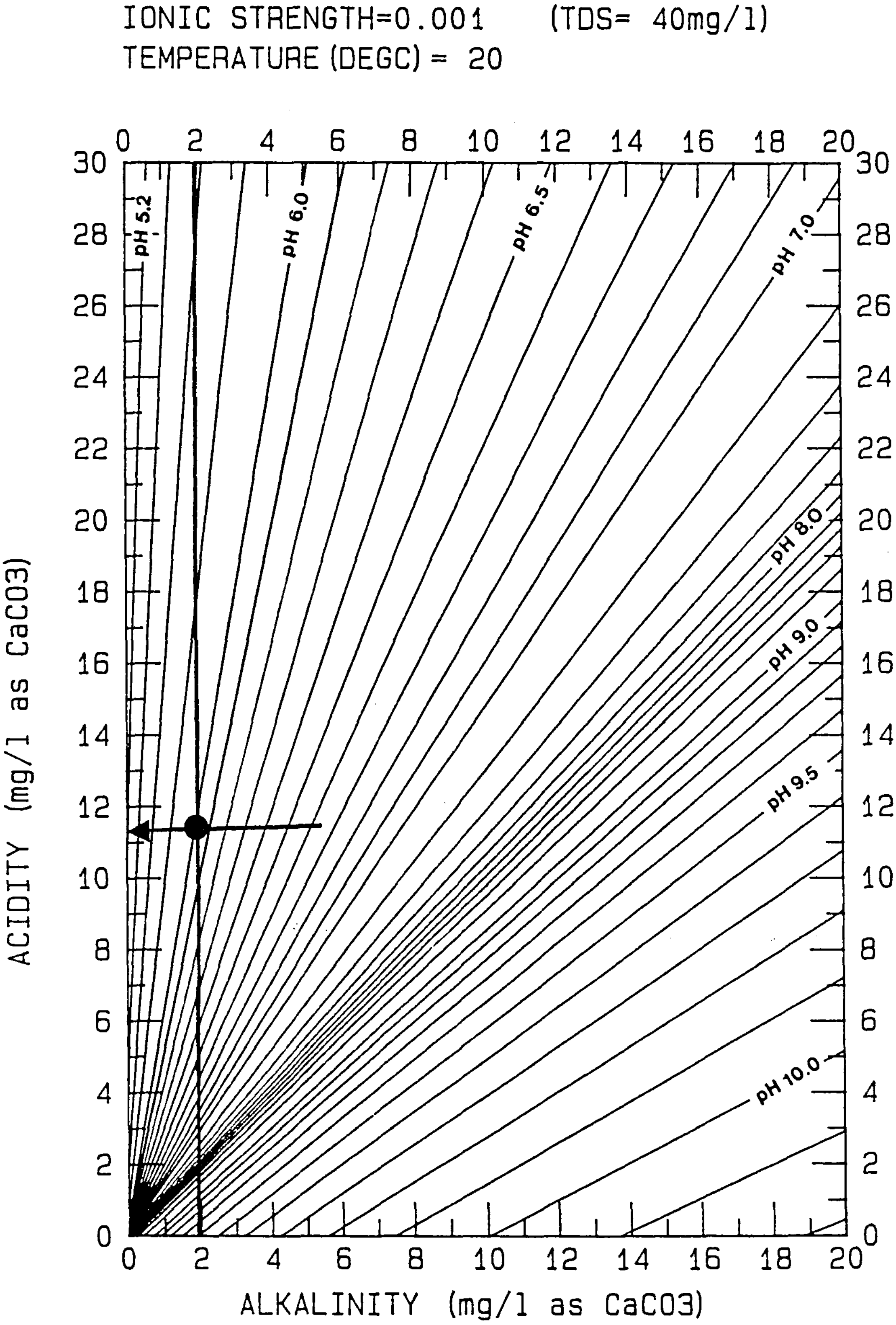


Fig 5.8 Example 7: Use of Deffeyes type diagram to determine Acidity. Alkalinity 2 mg/ℓ and pH 6,0 gives Acidity = 11 mg/ℓ.

We now have all the information to calculate the CO_2 dosage. It is determined from

Acid(final) = Acid(initial) - $Ca(OH)_2$ dosage + CO_2dosage
i.e.
CO_2 dosage = Acid(final) - Acid(initial) + $Ca(OH)_2$ dosage

where all species concentrations are expressed in mg/ℓ as $CaCO_3$.

(v) Final pH on leaving the plant, pH(final), is given by the value of the pH line through the intersection of the Alk(final) and Acid(final) plot lines on the MCL or the Deffeyes diagram.

(vi) The pH in the distribution system after precipitation of $CaCO_3$ to saturation has taken place, i.e. pH(sat), is given by the value of the pH line through the intersection of Alk(sat) and Acid(sat) lines in the MCL or Deffeyes diagram.

EXAMPLE 8: Stabilization of calcium and carbonate species deficient water

Analyses of water, after colour removal, gives Alkalinity 1 mg/ℓ, Ca^{2+} 5 mg/ℓ (both as $CaCO_3$), pH 5,8, total dissolved solids 40 mg/ℓ, i.e. ionic strength 0,001, and temperature 15°C. Determine $Ca(OH)_2$ and CO_2 dosages to stabilize the water, i.e. to adjust Alkalinity and calcium concentrations both to at least 50 mg/ℓ (as $CaCO_3$) when the water leaves the plant, and to adjust pH such that the water has a precipitation potential of 4 mg/ℓ $CaCO_3$.

(i) Choice of Deffeyes and MCL diagrams:

Select the Deffeyes and MCL diagrams from those listed in Appendices A and B respectively for μ = 0,001 and temperature 15°C, see Figs 5.9 and 5.10 respectively.

(ii) Determine the initial Acidity, Acid(initial):

On the Deffeyes diagram find the intersection of Alk = 1 mg/ℓ and pH 5,8, to give Acid(initial) = 11 mg/ℓ as $CaCO_3$,

(iii) $Ca(OH)_2$ dosage

Determine $Ca(OH)_2$ dosage to give Alkalinity and Ca^{2+} values each of at least 50 mg/ℓ as $CaCO_3$ on leaving the plant. Equation (5.2) applies, i.e.

$Ca(OH)_2$ dosage = Alk(final) - Alk(initial)
= 50 - 1
= 49 mg/ℓ as $CaCO_3$.

The corresponding Ca^{2+} concentration after dosing, Ca^{2+}(final), is

Ca^{2+}(final) = Ca^{2+}(initial) + $Ca(OH)_2$ dosage
= 5 + 49
= 54 mg/ℓ as $CaCO_3$.

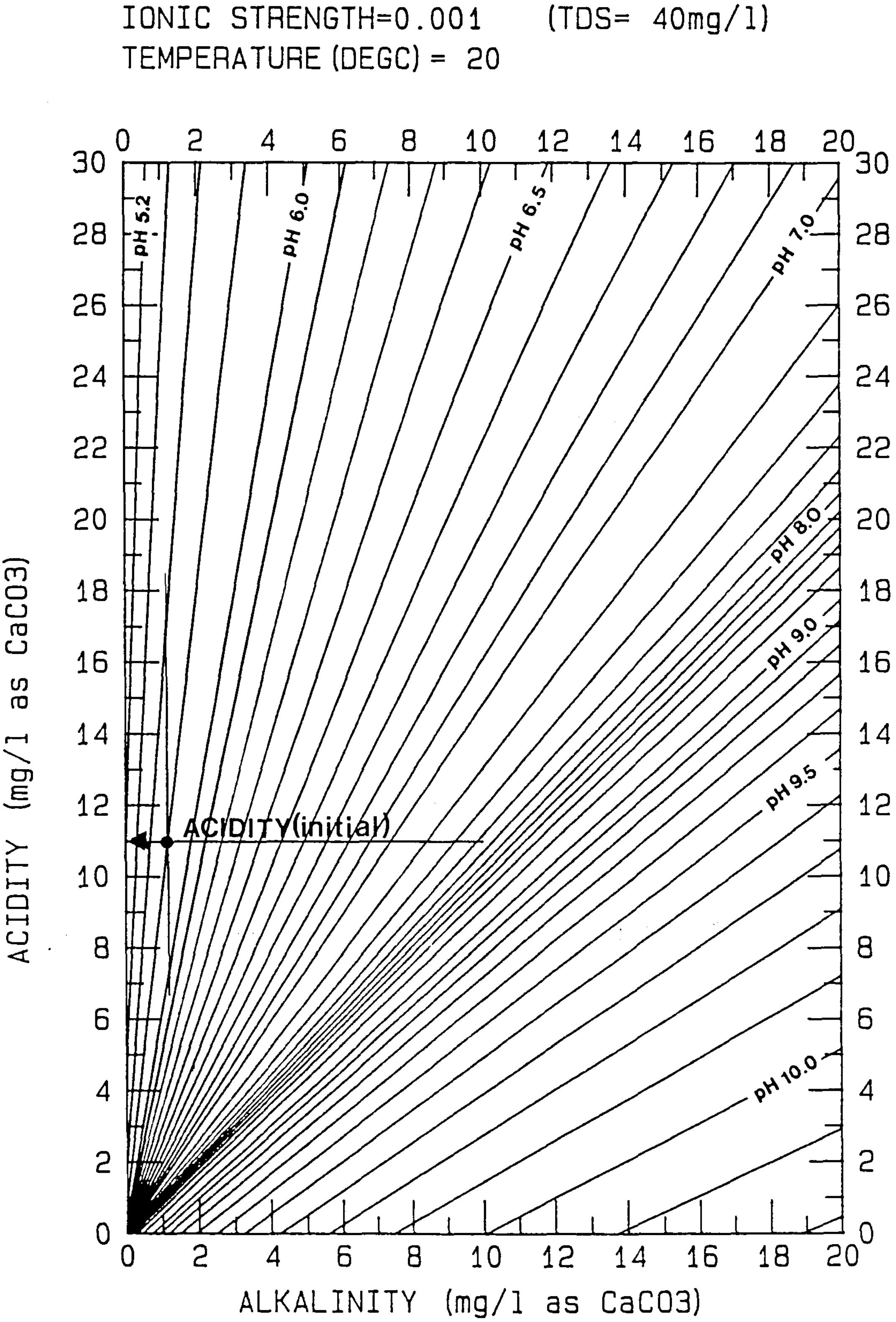


Fig 5.9 Example 8: Acidity determination for a carbonate species deficient water with Alk = 1 mg/ℓ and pH = 5,8. Acidity = 11 mg/ℓ.

Thus, the final state of the water on leaving the works must be

Alk(final) = 50 mg/ℓ as $CaCO_3$
Ca^{2+}(final) = 54 mg/ℓ as $CaCO_3$.

(iv) CO_2 dosage:

Determine the CO_2 dosage to give a pH(final) such that the water will be supersaturated with a precipitation potential of 4 mg/ℓ $CaCO_3$. The crux of this determination is to find the final Acidity of the water when it leaves the works, Acid(final).

From (iii) above we know that when the water leaves the plant it is supersaturated with a precipitation potential of 4 mg/ℓ $CaCO_3$. As Alk(final) = 50 mg/ℓ and Ca^{2+}(final) = 54 mg/ℓ, should precipitation take place, then for x mg/ℓ $CaCO_3$ precipitated, x mg/ℓ of each Alkalinity and Ca^{2+} are removed, i.e.

Alk(sat) = Alk(final) - x
Ca^{2+}(sat) = Ca^{2+}(final) - x.

Knowing the Alk(sat) and Ca^{2+}(sat) values we find Acid(sat) value from the Acidity ordinate value of the intersection of Alk(sat) and Ca^{2+}(sat) lines in the MCL diagram. Now the Acidity does not change with $CaCO_3$ dissolution or precipitation. Hence,

Acid(final) = Acid(sat).

In this rather roundabout way we determine the final Acidity value, Acid(final). The first two steps in this calculation are to determine calcium and Alkalinity values for the distribution water should all the calcium carbonate be precipitated to saturation from the supersaturated water, i.e.

Ca^{2+} at saturation, Ca^{2+}(sat):

Ca^{2+}(sat) = Ca^{2+}(final) - Ca^{2+} precipitation potential
= 54 - 4 = 50 mg/ℓ as $CaCO_3$

Alkalinity at saturation, Alk(sat):

Alk(sat) = Alk(final) - Alk. precipitated as $CaCO_3$

= 50 - 4 = 46 mg/ℓ as $CaCO_3$.

Acidity at saturation, Acid(sat):

The Acid(sat) value is given by the Acidity ordinate value of the intersection of the Alk(sat) = 46 mg/ℓ and Ca^{2+}(sat) = 50 mg/ℓ lines, see Point 1 in Fig 5.10, i.e.

$$\begin{aligned}\text{Acid(sat)} &= 45\ \text{mg}/\ell \\ &= \text{Acidity(final)}\end{aligned}$$

We now have all the information to calculate the CO_2 dosage. It is determined from

$$\text{Acid(final)} = \text{Acid(initial)} - Ca(OH)_2 \text{ dosage} + CO_2 \text{ dosage}$$

i.e.

$$\begin{aligned}CO_2 \text{ dosage} &= \text{Acid(final)} - \text{Acid(initial)} + Ca(OH)_2 \text{ dosage} \\ &= 45 - 11 + 49 = 83\ \text{mg}/\ell \text{ as } CaCO_3\end{aligned}$$

(v) Final pH on leaving the works:

pH(final) is given by the value of the pH line through the intersection of Alk(final) and Acid(final) plot lines on the MCL diagram, i.e. Point 2 with pH(final) = 9,1.

(vi) Saturated pH value:

The pH in the distribution system after saturation is attained due to precipitation of 4 mg/ℓ $CaCO_3$, is given by the value of the pH line through the intersection of Alk(sat) and Acid(sat) lines in the MCL diagram, i.e. Point 1 with pH(sat) = 8,67.

We summarize the stabilization dosages and products for this water as follows:**

	Water before stabilization	Water leaving works*	Water after precipitation in distribution system
Alkalinity	1	50	46
Acidity	11	45	45
pH	5,8	9,1	8,67
Ca^{2+}	5	54	50
Precipitation potential	-15	+4	0

* Chemical dosages: $Ca(OH)_2$ = 49 mg/ℓ as $CaCO_3$
CO_2 = 83 mg/ℓ as $CaCO_3$

** All concentrations in mg/ℓ expressed as $CaCO_3$

5.4 SOFTENING OF HARD WATERS

Waters are referred to as 'hard' or 'soft' depending on the concentration of dissolved divalent metallic cations. Classification of water supplies in terms of 'degree of hardness' is summarized in Table 5.9 after Kunin (1972).

In natural terrestial waters the hardness species are comprised virtually totally of Ca^{2+} and Mg^{2+} ions. Consequently, in this text 'hardness' will refer to the sum of the concentrations of Ca^{2+} and Mg^{2+} species, and, following general convention, will be expressed

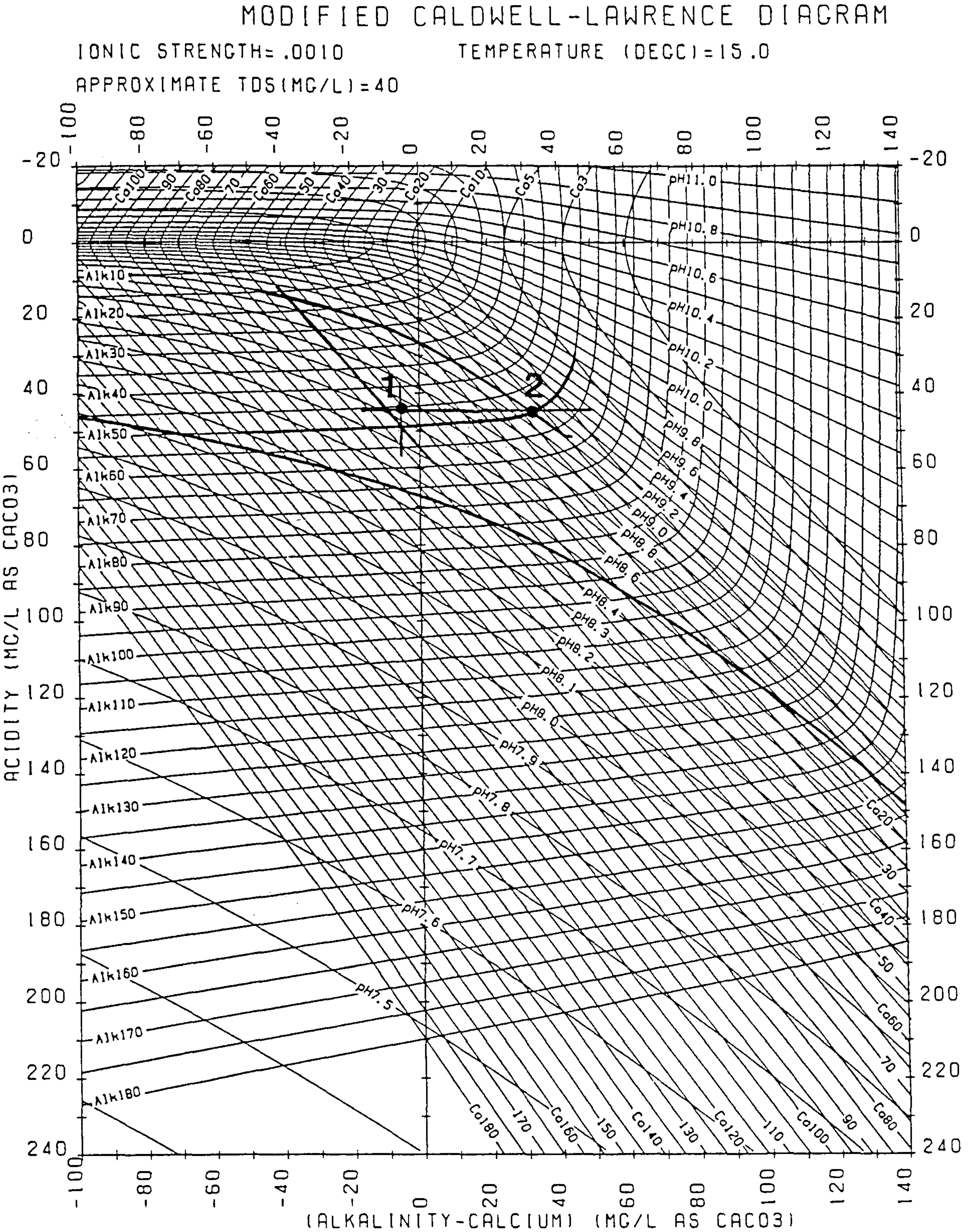


Fig 5.10 Example 8: Chemical dosage determination for stabilization of calcium carbonate species deficient water to Alk 50 mg/ℓ, Ca^{2+} 54 mg/ℓ and pH 9,1 to give precipitation potential = 4 mg/ℓ $CaCO_3$.

on the calcium carbonate concentration scale, i.e. mg/ℓ as $CaCO_3$.

Waters containing appreciable hardness are not suitable for many industrial purposes. Also, excessively hard waters can be unacceptable for household use. Such waters need to be 'softened', i.e. the concentrations of Ca^{2+} and Mg^{2+} species need to be reduced to acceptable levels. For industrial purposes the acceptable level will depend on the particular industry; for household use a hardness of less than 120 mg/ℓ as $CaCO_3$ is usually acceptable, Kunin (1972). Furthermore, subsequent to the softening process the water needs to be stabilized to prevent aggression, corrosion and excessive post precipitation.

Although Ca^{2+} and Mg^{2+} usually are removed simultaneously in the same unit process, it is instructive to deal separately with Ca^{2+} and (Ca^{2+} + Mg^{2+}) removal.

Calcium removal in municipal or other bulk water treatment works is usually by precipitation as solid $CaCO_3$. The pH is raised by addition usually of $Ca(OH)_2$, whereupon the bicarbonate species, HCO_3^-, predominant in the pH range 6,5 to 10, is changed to CO_3^{2-} the predominant species at pH > 10. When the species concentration product $[Ca^{2+}][CO_3^{2-}]$ exceeds the apparent solubility product constant, K'_{sp}, $CaCO_3$ precipitates until the species concentration product equals the apparent solubility product. The softening process reduces the Alkalinity, Acidity, total carbonate species and Ca^{2+} concentrations. If the $Ca(OH)_2$ dose is appropriately selected and the precipitation reaction can go to completion, by letting the reaction take place in a slurry of precipitant, the final state of the water (pH, Alkalinity and Ca^{2+} concentration) will be at or near saturation and perhaps in a pH region still acceptable for general distribution so that after separation of the water and slurry, no additional treatment may be necessary to satisfy the criteria to prevent aggression and pacify corrosion.

Table 5.9 Hardness classification of waters (after Kunin, 1972).

Hardness range (mg/ℓ as $CaCO_3$)	Description
0-60	Soft
61-120	Moderately hard
121-180	Hard
>180	Very hard

Magnesium ions are removed by precipitation of solid magnesium hydroxide, $Mg(OH)_2$. By addition of $Ca(OH)_2$, the OH^- concentration is raised corresponding to a pH of 11 or more whereupon the species concentration product $[Mg^{2+}][OH^-]^2$ exceeds the apparent solubility product, K'_{spm}, and $Mg(OH)_2$ precipitates until $[Mg^{2+}][OH^-]^2 = K'_{spm}$ is established. When $Ca(OH)_2$ is added gradually to a slurry of precipitant and water containing Ca^{2+} and Mg^{2+}, first $CaCO_3$ precipitates until at a pH of about 10 virtually all the total carbonate species content is removed by $CaCO_3$ precipitation. Further addition of $Ca(OH)_2$ increases OH^- and Ca^{2+} until $Mg(OH)_2$ precipitates which removes Mg^{2+} and OH^- species but not Ca^{2+} species. Thus when Mg^{2+} has been removed one has a water with a Ca^{2+} content of about 200 mg/ℓ (expressed as

$CaCO_3$) or more, with virtually no carbonate species, at a pH of 11 or higher. This calcium cannot be removed adequately by CO_2 dosing, only. Consequently CO_3^{2-} ions are added, by dosing Na_2CO_3 to the slurry until the Ca^{2+} concentration is at an acceptable level. Thereafter the water is separated from the slurry, CO_2 is added to the water to reduce the pH, increase the total carbonate species concentration and satisfy the criteria for prevention of aggression and pacification of corrosion.

Calculation of the dosages of $Ca(OH)_2$ and Na_2CO_3 for softening and CO_2 for stabilization is a simple procedure using the Modified Caldwell-Lawrence diagram. Furthermore, on the chart the changes in equilibrium states with chemical dosing provide a visual description of the chemical changes taking place.

The MCL diagram adequately describes the interdependence between the maximum Ca^{2+} content for $CaCO_3$ saturation and the carbonate species concentrations (via Alkalinity or Acidity) and pH. However, up to now, the maximum Mg^{2+} content for $Mg(OH)_2$ saturation has not been addressed in the diagram. For softening purposes the maximum concentration for Mg^{2+} in water is governed by the solubility product for $Mg(OH)_2$, i.e. from Eq (4.42) at saturation,

$$(Mg^{2+})(OH^-)^2 = K_{spm}.$$

In terms of species concentrations, this equation

$$[Mg^{2+}]_s[OH^-]^2 = K_{spm}/(f_D.f_M^2) = K'_{spm}.$$

Where subscript 's' = magnesium species concentration at saturation with respect to $Mg(OH)_2$.

and, the maximum Mg^{2+} concentration at saturation Mg_s^{2+} is

$$[Mg^{2+}]_s = K'_{spm}/[OH^-]^2 \qquad (5.\ 4)$$

Now, from Eq (4.1), pH = $-\log_{10}(H^+) = -\log_{10}(K'_w/[OH^-])$, hence derive an equation for $[Mg^{2+}]_s$ in terms of pH (a parameter easily measured), i.e. solving for $[OH^-]$ from Eq (4.1) substituting into Eq (5.2) and simplifying

$$[Mg^{2+}]_s = K'_{spm}.10^{-2pH}/K'_w \qquad (5.\ 5)$$

or, for the concentration of Mg^{2+} on the $CaCO_3$ scale,

$$Mg_s^{2+} = (K'_{spm}.10^{-2pH}/K'_w).10^5 \quad (5.\ 6)$$

Thus, for each pH there is some limiting maximum concentration of Mg^{2+} which cannot be exceeded without $Mg(OH)_2$ precipitating.

In each of the MCL diagrams is a nomogram based on Eq (5.6) relating maximum concentration of Mg^{2+} (expressed on the $CaCO_3$ scale) with pH for the temperature and ionic strength of the particular diagram.

5.4.1 Dosage estimation for softening

Softening is carried out in the presence of a high concentration of precipitant; for softening dosage estimation purposes it can be accepted that the water will be saturated with respect to the mineral precipitant before and after dosing.This simplifies dosage calculations in the MCL diagram, because, for any (saturated) water only the effects of dosage on the axis parameters, (Alk-Ca) and Acidity, need be considered. These effects in MCL diagram are briefly outlined below, for an in-depth analysis the reader is referred to Loewenthal and Marais, 1976.

For a water known to be saturated with respect to $CaCO_3$, the chemical characteristics of the water plot at a point in the MCL diagram, that is, lines representing Ca^{2+}, Alkalinity, pH, Acidity and (Alk-Ca) all intersect at a single point, the saturated state point; for the saturated condition, values for any two of these five parameters define the saturated equilibrium state of the water in the diagram, in particular, the axes parameters Acidity and (Alk-Ca). Consequently, to determine changes in the saturated state due to chemical dosing, we need to know only the effects of dosing on Acidity and (Alk-Ca), the values of which are unaffected by $CaCO_3$ precipitation or dissolution. These changes are very simple, from Eqs (4.38 to 4.40):

(i) Due to $Ca(OH)_2$ addition:

ΔAcidity = $-Ca(OH)_2$ added (on the $CaCO_3$ scale)
Δ(Alk-Ca) = 0.

That is, the saturated state point moves vertically in the diagram a distance equal to the $Ca(OH)_2$ added (on the $CaCO_3$ scale).

(ii) Due to Na_2CO_3 addition:

ΔAcidity = 0
Δ(Alk-Ca) = Na_2CO_3 added (on the $CaCO_3$ scale).

That is, the saturated state point moves horizontally to the right in the MCL diagram due to Na_2CO_3 addition.

(iii) Due to $Mg(OH)_2$ precipitation:

ΔAcidity = $Mg(OH)_2$ precipitated (on the $CaCO_3$ scale)
Δ(Alk-Ca) = $-Mg(OH)_2$ precipitated.

That is, the saturated state point moves at 45° downwards to the left (relative to the axes) a distance equal to root two (1,414) times the mass concentration of $Mg(OH)_2$ precipitated (on the $CaCO_3$ scale).

For the purposes of dosing calculations for softening, consideration of the effects of the three dosing chemicals above is sufficient.

EXAMPLE 9: Calcium softening

Analyses of a water gives Alk 300 mg/ℓ, Ca^{2+} 280 mg/ℓ (both as $CaCO_3$), pH 7,2, TDS 400 mg/ℓ (μ = 0,01) and temperature 20°C. Determine the $Ca(OH)_2$ dosage to soften the water to Ca^{2+} 100 mg/ℓ.

Dosage determination is carried out in the following steps:

(i) Modified Caldwell-Lawrence (MCL) diagram:

From the MCL diagrams listed in Appendix B select that for ionic strength 0,01 and temperature 20°C, see Fig 5.11.

(ii) Determine the initial Acidity and (Alk-Ca) of the water:

Plot in the diagram lines representing measured values for Alkalinity and pH. These lines intersect at Point 1. The Acidity ordinate value of Point 1 gives initial Acidity of the raw water, i.e. 390 mg/ℓ as $CaCO_3$.

Initial(Alk-Ca) = (300 - 280)
= 20 mg/ℓ.

(iii) Determine the initial saturated state point:

Plot in the diagram the lines for initial Acidity 390 mg/ℓ and (Alk-Ca) = 20 mg/ℓ. Intersection of these lines occurs at Point 2. The initial saturated state the water will attain is given by values of lines for Alkalinity, Ca^{2+} and pH through Point 2. This initial saturated condition will occur naturally through contact of the raw water with the $CaCO_3$ slurry in the softener.

(iv) Determine $Ca(OH)_2$ dosage to soften the water to Ca^{2+} 100 mg/ℓ:

Addition of $Ca(OH)_2$ has no effect on (Alk-Ca); that is after softening (Alk-Ca) equals the initial value. Consequently, intersection of lines for (Alk-Ca) = 20 mg/ℓ and Ca^{2+} 100 mg/ℓ gives the saturated state equilibrium point after softening, i.e. Point 3 with Acidity 120 mg/ℓ. The $Ca(OH)_2$ dosage required to effect softening is the difference in Acidity between the initial condition (i.e. Acidity of either Points 1 or 2) and the final condition (i.e. Acidity Point 3). That is

$Ca(OH)_2$ dosage = Acidity(initial) - Acidity(final)
= 390 - 120
= 270 mg/ℓ (as $CaCO_3$).

In the example above, if there is complete precipitation, the final condition of the water will be the saturated state point, Point 3. Alkalinity, Ca^{2+} and pH values will be the values for the respective lines through Point 3, i.e. Alkalinity 120 mg/ℓ, Ca^{2+} 100 mg/ℓ and pH 7,95. After separation of the water and slurry, the water would need to be treated with a small amount of $Ca(OH)_2$ to attain a precipitation potential of about 5 mg/ℓ $CaCO_3$. Alternatively, if the hydraulic retention time in the softening unit is too short, or the slurry concentration too low, the effluent might be still in a slightly supersaturated state with a precipitation potential of about 5 mg/ℓ $CaCO_3$. This can be verified for the applied $Ca(OH)_2$ dosage, determined in (iv) above, if the reactor is maintained in either of the following states:

(a) Ca^{2+} concentration is 105 mg/ℓ, or

(b) Alkalinity is 125 mg/ℓ, or

(c) pH = 8,1, i.e. the pH value through the intersection point of Alkalinity 125 and Acidity 120 mg/ℓ.

In this example the water contained only Ca^{2+} hardness. Usually such waters will contain both Ca^{2+} and Mg^{2+} hardness. One can still, of course, remove the Ca^{2+} only and determine the $Ca(OH)_2$ dosage as above. However, when Ca^{2+} is precipitated, and not Mg^{2+} as well, the $[Mg^{2+}]/[Ca^{2+}]$ ratio increases as the precipitation proceeds and when it exceeds about unity the solubility product constant for $CaCO_3$ tends to increase (pK_s decreases) due to incorporation of Mg^{2+} ions into the $CaCO_3$ crystal lattice. This has the effect that the final Ca^{2+} concentration after precipitation is slightly higher than that predicted by the calculation procedure above, Benjamin, Loewenthal and Marais (1977). The observation is for information only, from a practical point of view it should not affect the softening attained to any significant extent.

EXAMPLE 10: Calcium and magnesium softening

Analyses of water gives: Alkalinity 130 mg/ℓ, Ca^{2+} 230 mg/ℓ, Mg^{2+} 40 mg/ℓ (all as $CaCO_3$), pH 7,3, ionic strength 0,01 and temperature of 20°C. Determine the dosages of $Ca(OH)_2$, and soda ash, Na_2CO_3, to soften the water to Ca^{2+} 60 mg/ℓ and Mg^{2+} 4 mg/ℓ (both as $CaCO_3$); assume that the softening process occurs in a reactor with a high concentration of mineral precipitant present.

Dosage calculations using the MCL diagram are carried out in the following steps:

(i) Modified Caldwell Lawrence (MCL) diagram:

From the MCL diagrams listed in Appendix B select that for ionic strength 0,01 and temperature of 20°C, see Fig 5.12.

(ii) Determine the initial Acidity and (Alk-Ca) of the raw water:

Plot in the diagram lines representing measured values for pH and Alkalinity. These lines intersect at Point 1. The Acidity value of Point 1 gives initial Acidity of the raw water, i.e. Acidity 160 mg/ℓ.

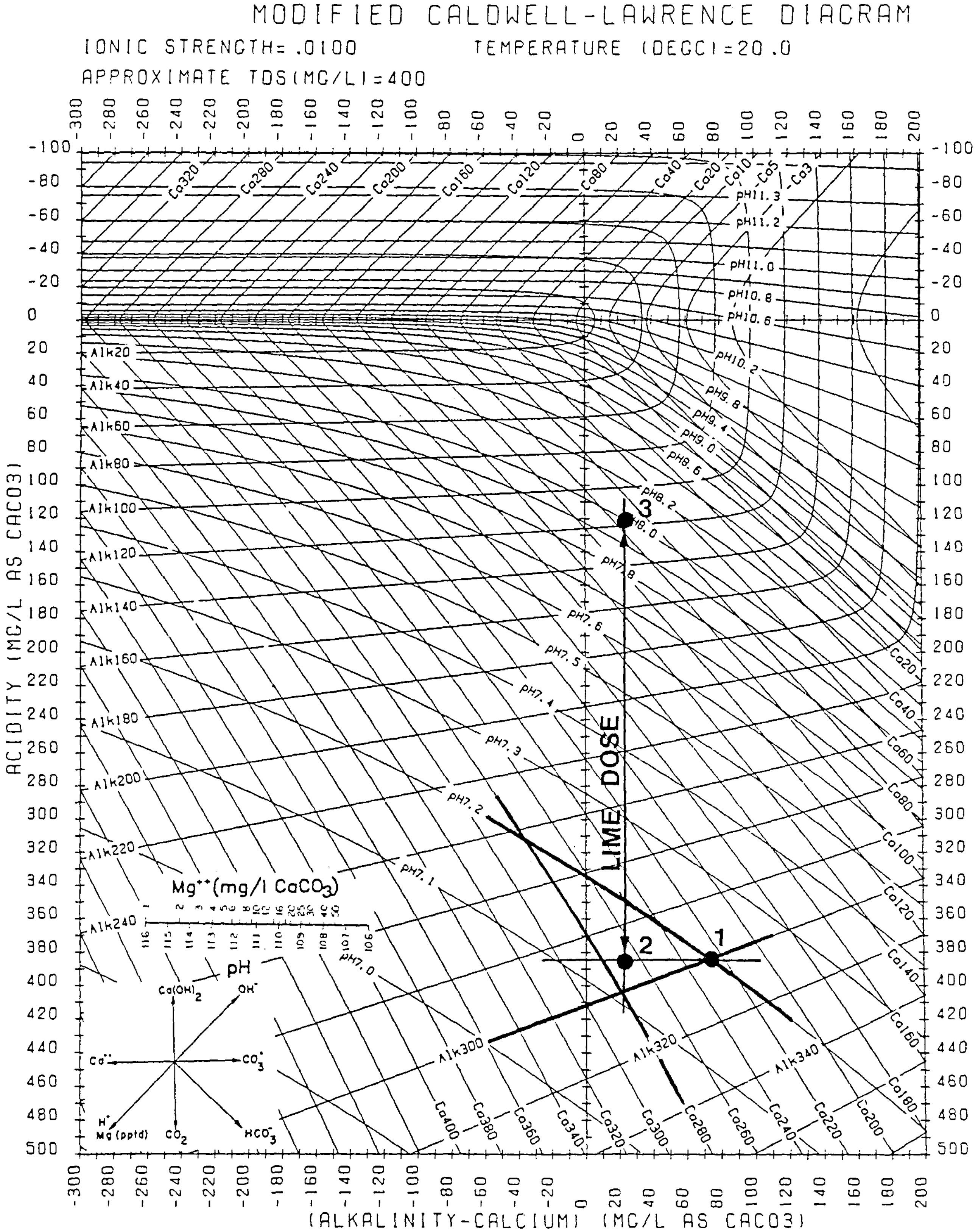


Fig 5.11 Example 9: Determination of lime dosage for calcium softening.

Initial (Alk-Ca) = (130 - 230) = -100 mg/ℓ.

(iii) Determine initial saturated state point:

Plot in the diagram the lines for initial Acidity (160 mg/ℓ) and (Alk-Ca) = -100 mg/ℓ. Intersection of these lines occurs at Point 2. The initial saturated state which the water would attain with time is given by the values of lines for Alkalinity, Ca^{2+} and pH through Point 2.

(iv) Determine the pH value such that the water is saturated with respect to $Mg(OH)_2$ with Mg^{2+} = 4 mg/ℓ:

Referring to the monogram of Mg_s^{2+} versus pH in Fig 5.12, at pH 10,8 the water is just saturated with 40 mg/ℓ Mg^{2+} (as mg/ℓ $CaCO_3$). Increasing pH above 10,8 causes precipitation of $Mg(OH)_2$.

Final stipulated magnesium concentration is 4 mg/ℓ (as $CaCO_3$). The Mg_s^{2+} - pH nomogram in Fig 5.12 shows that at $Mg(OH)_2$ saturation with pH 11,3 the maximum concentration of Mg^{2+} in the water is 4 mg/ℓ. Thus, in this problem, after precipitating (40-4) = 36 mg/ℓ $Mg(OH)_2$ (as $CaCO_3$) we require a pH of 11,3.

(v) Determine the saturated state point in the diagram after precipitation of 36 mg/ℓ $Mg(OH)_2$:

In the conditioning diagram draw the line representing the pH value at which the water is just saturated with the final desired Mg^{2+} concentration, at pH 11,3 the water is just saturated with 4 mg/ℓ Mg^{2+} (as $CaCO_3$).

Precipitation of 36 mg/ℓ $Mg(OH)_2$ (as $CaCO_3$) causes the (Alk-Ca) ordinate value to change by -36 mg/ℓ, thus,

(Alk-Ca) after $Mg(OH)_2$ precipitation
= (Alk-Ca) initial - $Mg(OH)_2$ precipitated
= (-100) - 36 = -136 mg/ℓ.

Intersection of lines for (Alk-Ca) = -136 and pH 11,3 occurs at Point 3. This is the saturated state point after $Ca(OH)_2$ dosing and $Mg(OH)_2$ precipitation with Acidity = 76 mg/ℓ and Alkalinity = 78 mg/ℓ (both as $CaCO_3$). The condition just prior to $Mg(OH)_2$ precipitation is given by 45° line from Point 3 to the intersection of (Alk-Ca) = -100, viz Point 3'.

(vi) Calculate $Ca(OH)_2$ dosage to effect the $Mg(OH)_2$ precipitation:

The $Ca(OH)_2$ dosage to effect precipitation of 36 mg/ℓ $Mg(OH)_2$ is given by the sum of the changes in Acidity due to dosing and $Mg(OH)_2$ precipitation. That is, the change in Acidity between Points 1 and 3 results from two effects, (a) $Ca(OH)_2$ dosing which decreases the initial Acidity, and (b) $Mg(OH)_2$ precipitation which increases Acidity by the mass concentration of $Mg(OH)_2$ precipitated, i.e.

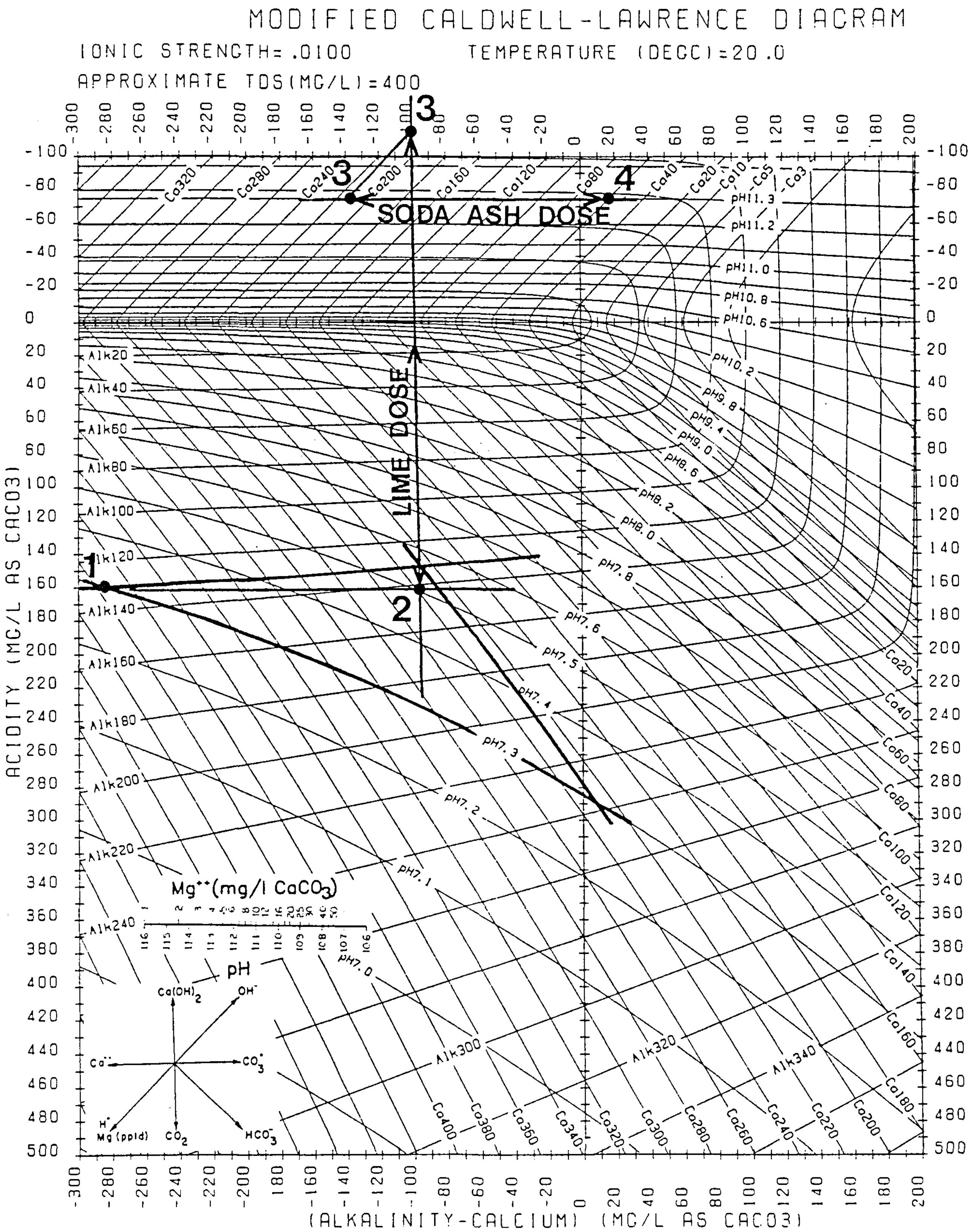


Fig 5.12 Example 10: Calcium and magnesium softening using lime and soda ash.

Acidity change = - $Ca(OH)_2$ dosage + $Mg(OH)_2$ precipitated
i.e.
Acidity(3) - Acidity(1) = - $Ca(OH)_2$ dosage + $Mg(OH)_2$ precipitated
i.e.
$Ca(OH)_2$ dosage = {Acidity(1) - Acidity(3)} + $Mg(OH)_2$ precipitated
= {160 - (-76)} + 36 = 272 mg/ℓ (as $CaCO_3$).

At Point 3 the Ca^{2+} concentration now is 214 mg/ℓ as $CaCO_3$. The total carbonate species concentration, C_T, is obtained from Eq 4.21 i.e.

C_T = (Alkalinity + Acidity)/2
= [78 + (-76)]/2
= 1 mg/ℓ as $CaCO_3$.

Compare the C_T with the initial saturated C_T value (Point 2), which gives (140 + 160)/2 = 150 mg/ℓ as $CaCO_3$, and it is clear that after Mg^{2+} removal virtually all the C_T has been removed and water is virtually a slaked $Ca(OH)_2$ solution but with a higher Ca^{2+} concentration due to OH^- removal during Mg^{2+} precipitation.

(vii) Sodium carbonate dosage to effect Ca^{2+} softening:

Ca^{2+} concentration (given by Ca^{2+} value of Point 3, Fig 5.11) is now 214 mg/ℓ, a final Ca^{2+} value of 60 mg/ℓ is specified. Noting that Na_2CO_3 dosing does not affect Acidity, the final saturated condition of the water after Ca^{2+} precipitation is given by the intersection point of lines for Acidity = -76 mg/ℓ and Ca^{2+} = 60 mg/ℓ, i.e. Point 4.

The required Na_2CO_3 dosage is thus the difference in (Alk-Ca) between Points 3 and 4,

Na_2CO_3 dosage = $(Alk\text{-}Ca)_4$ - $(Alk\text{-}Ca)_3$
= 20 - (-136) = 156 mg/ℓ as $CaCO_3$.

The corresponding C_T value remains virtually the same as that at Point 4 i.e. 4 mg/ℓ as $CaCO_3$.

In the example above, after softening the pH of the water is 11,3. Clearly this value is too high for general municipal distribution, and the water must be stabilized. This aspect is considered in the following section.

An alternate way of visualizing the softening process shown in Fig 5.12 is as follows:

Addition of $Ca(OH)_2$ moves the saturated equilibrium Point 2 vertically (decreases Acidity) along a constant (Alk-Ca) path.

Precipitation of $Mg(OH)_2$ causes equal increase in Acidity and decrease (Alk-Ca) by an amount equal to the mass concentration of $Mg(OH)_2$ precipitated.

Knowing the mass of $Mg(OH)_2$ to be precipitated one can establish Point 3 as in (iv) above. Thus, a $CaCO_3$ saturated state point can be established in the diagram for the condition after $Ca(OH)_2$ dosage but before $Mg(OH)_2$ precipitation. This point, Point 3', will be vertically above Point 2 and at 45° up to the right from Point 3.

$Ca(OH)_2$ dosage = Acidity(Point 2) - Acidity (Point 3')
= 160 - (-112) = 272 mg/ℓ (as $CaCO_3$).

5.5 POST SOFTENING STABILIZATION

After calcium and magnesium softening, the slurry is passed through a settling tank where the water is separated from the sludge (precipitate). The clarified water retains the same pH as that of the slurry in the softening reactor, i.e. pH > 11 (see Fig 5.12) and has the Ca^{2+} concentration required for discharge to the distribution system. However, the water contains virtually no carbonate species and the pH is too high for potable use. Carbonate species are added and pH is lowered by dosing the clarified water with CO_2. Assuming for the moment that no $CaCO_3$ precipitates then CO_2 dosing adds Acidity but does not change Alkalinity, see Eqs (4.38 and 4.39). Thus, the Alkalinity and calcium, and hence (Alk-Ca), values remain constant. In the MCL diagram (Fig 5.12) with addition of CO_2 the Acidity ordinate moves vertically downwards from Point 4, (Alk-Ca) remains constant equal to the value through Point 4. Now the constant Ca^{2+} and Alkalinity lines through Point 4 curve down and intersect again on the constant (Alk-Ca) line. At the point of intersection the pH is the one at saturation now in the pH region acceptable for distribution; the change in Acidity between Point 4 and the final saturated point gives the CO_2 dosage. Usually this total CO_2 dosage is not added, but slightly less so that the water is slightly supersaturated. If the CO_2 is dosed in a completely mixed reactor and pH maintained constant at the lower value, no precipitation will take place. However, in a batch sample, if the CO_2 is added slowly so that the pH gradually decreases from the initial value of pH ≈ 11,3, $CaCO_3$ precipitation occurs and the saturated equilibrium point moves vertically down the (Alk-Ca) line until Acidity = 0 is reached, thereafter dissolution of the precipitated $CaCO_3$ occurs.

EXAMPLE 11: Post softening stabilization

The slurry mixture from the Ca^{2+} and Mg^{2+} softening unit in the previous example, Example 10 is clarified. Analyses of the clarified supernatant water is from Point 4, Fig 5.12, Alkalinity 76 mg/ℓ, Ca^{2+} 60 mg/ℓ, pH 11,3, TDS 400 mg/ℓ and temperature 20°C.

Determine pH and CO_2 requirements to obtain a precipitation potential of 5 mg/ℓ $CaCO_3$ and a pH in the region 6,5 < pH < 9,5. Calculations are carried out in the following sequence:

(i) Modified Caldwell-Lawrence (MCL) diagram:

Select the MCL diagram from those listed in Appendix B with TDS 400 mg/ℓ (μ = 0,01) and temperature 20°C, see Fig 5.13. (In this case the diagram is the same as that in Fig 5.12 except that the scale is bigger.)

(ii) Initial saturated state of the water:

Sketch in the diagram those lines representing initial Alkalinity, pH and Ca^{2+} of the water. These lines all intersect at Point 4. Consequently the initial Acidity is the Acidity ordinate value of Point 4, i.e. initial Acidity = -76 mg/ℓ.

(iii) Determine the CO_2 dosage to give a pH(final) such that the water will have a precipitation potential of 5 mg/ℓ $CaCO_3$:

The crux of this determination is to find the final Acidity of the water when it leaves the works, Acid(final).

We know that when the water leaves the plant it must be supersaturated with a precipitation potential of 5 mg/ℓ $CaCO_3$. As Alk(final) = 80 mg/ℓ and Ca^{2+}(final) = 60 mg/ℓ, should $CaCO_3$ precipitation occur, then for x mg/ℓ $CaCO_3$ precipitated, x mg/ℓ of each Alkalinity and Ca^{2+} are removed, i.e.

Alk(sat) = Alk(final) - x
Ca(sat) = Ca^{2+}(final) - x.

Knowing Alk(sat) and Ca(sat) values we find Acidity(sat) from the Acidity ordinate value of the intersection of Alk(sat) and Ca(sat) lines in the MCL diagram. Now the Acidity does not change with $CaCO_3$ dissolution or precipitation. Hence,

Acid(final) = Acid(sat)

Ca^{2+} at saturation, Ca^{2+}(sat):

Ca^{2+}(sat) = Ca^{2+}(final) - Ca^{2+} precipitation potential
= 60 - 5 = 55 mg/ℓ as $CaCO_3$.

Alkalinity at saturation, Alk(sat):

Alk(sat) = Alk(final) - Alk. precipitation potential
= 80 - 5 = 75 mg/ℓ as $CaCO_3$.

Acidity at saturation, Acid(sat):

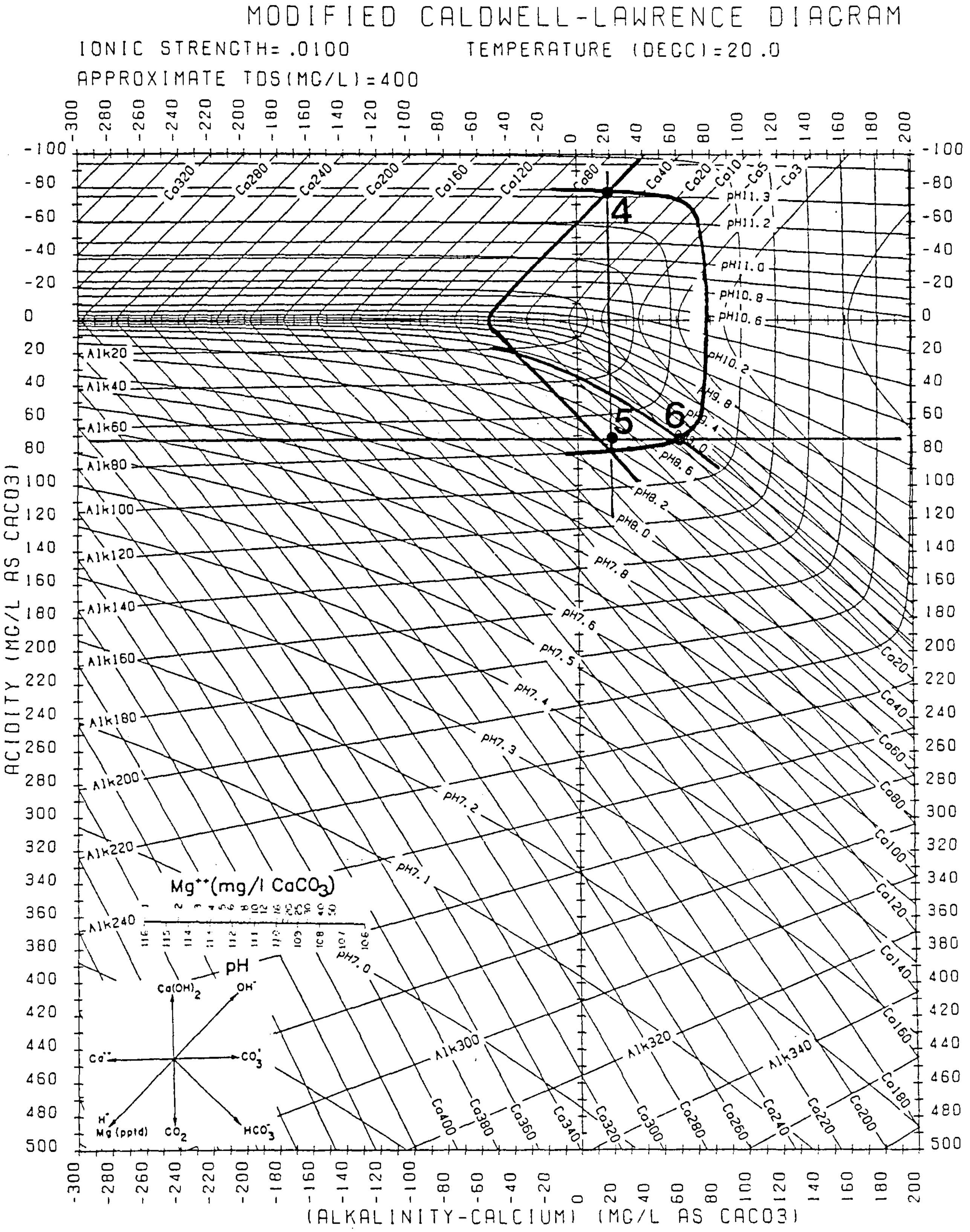
The Acid(sat) value is given by the Acidity ordinate value of the intersection of Alk(sat) = 75 mg/ℓ and Ca(sat) = 55 mg/ℓ lines, see Point 5, Fig 5.13, i.e.

Acid(sat) = 71 mg/ℓ
= Acid(final)

Now we have all the information to calculate the CO_2 dosage. It is determined from

Acid(final) = Acid(initial) + CO_2 dosage

i.e.



<u>Fig 5.13</u> Example 11: Post softening stabilization for recarbonation with CO_2 gas.

CO_2 dosage = Acid(final) - Acid(initial)
= 71 - (-76)
= 147 mg/ℓ as $CaCO_3$.

(iv) Final pH on leaving the works:

pH(final) is given by the value of the pH line through the intersection of Alk(final) and Acid(final) plot lines on the MCL diagram, i.e. Point 6 with pH 8,9.

5.6 WATERS WITH EXCESS DISSOLVED CARBON DIOXIDE

Expulsion of CO_2 from water to the air is of particular importance in water treatment when dealing with waters derived from underground sources. For these waters the in situ dissolved CO_2 content usually is very high compared with waters in contact with the air. When pumped to surface and exposed to the air the difference in partial pressure between air and water creates a driving force for CO_2 expulsion from the water. Carbon dioxide expulsion causes the pH to increase, and, depending on the dissolved calcium content, the apparent solubility product for $CaCO_3$ may be exceeded whereupon $CaCO_3$ precipitates. This may cause severe scaling and narrowing of pipe diameters, and turbid effluents with high $CaCO_3$ suspended solids content, see Section 4.4. Whereas equilibrium between species in the aqueous phase is virtually instantaneous, when two or more phases, aqueous, gas and solid, are present the rate to equilibrium between phases is governed by physico-chemical factors in the water body and is usually relatively slow. For example, the rate to equilibrium between dissolved carbonate species and CO_2 in the air is dependant on the difference in partial pressure and mixing conditions; the rate of equilibrium attainment between the solid $CaCO_3$ and the aqueous Ca^{2+} and CO_3^{2-} ions is dependant on the solid surface area and the degree of supersaturation. In consequence, an underground water when brought to the surface will lose CO_2 to the air and precipitate $CaCO_3$ out of solution in varying degrees and rates depending upon the specific physical conditions:

(i) If the water is exposed to the air for a relatively brief period before entering a closed conduit system, CO_2 expulsion will be limited and depending upon the Ca^{2+} content and the pH in the exposed water, a state of supersaturation will be induced. If the supersaturation is not too high, precipitation may not occur or be limited. If sufficiently high, precipitation as dispersed $CaCO_3$ solids may take place in the water or solid precipitant scale may form on the conduit walls. Once $CaCO_3$ saturation is re-established no further precipitation can take place even though the water is still supersaturated with respect to the CO_2 in the air because the water in the pipe is sealed from contact with the air.

(ii) If the water is transported in an open channel, CO_2 exchange will take place until equilibrium with CO_2 in the air is established. The loss of CO_2 will raise the pH, and if sufficient Ca^{2+} is present, the apparent solubility product for $CaCO_3$ will be exceeded and $CaCO_3$ solid precipitated out of solution. The rate of precipitation will be determined by a complex set of interacting conditions between CO_2 loss, pH changes,

$CaCO_3$ precipitation potential and crystal surface available. However, what is certain is that over a length of the channel eventually a three phase equilibrium condition will be established whereupon precipitation will cease.

In both the cases above it will be useful to form estimates of the changes that can be expected in the water and the masses of precipitant that may form.

EXAMPLE 12: CO_2 expulsion from underground water pumped to surface

Analyses of an underground water pumped to surface gives Alkalinity 320 mg/ℓ, Ca^{2+} 210 mg/ℓ, pH 7,4, TDS 800 mg/ℓ (i.e. ionic strength 0,02) and temperature of 15°C. The water is exposed to the air. Determine the new chemical state of the water, the $CaCO_3$ precipitation potential and the mass concentration of CO_2 expelled to the air if (a) CO_2 equilibrium is attained rapidly with the air and no $CaCO_3$ precipitation occurs during CO_2 exchange but can occur after the water is isolated from the air, and (b) CO_2 equilibrium is attained relatively slowly and $CaCO_3$ precipitation takes place simultaneously.

(a) Rapid CO_2 loss with no associated $CaCO_3$ precipitation during CO_2 exchange

(i) Modified Caldwell-Lawrence (MCL) diagram:

Select the MCL diagram from those listed in Appendix B with ionic strength 0,02 and temperature 15°C, see Fig 5.14.

(ii) Establish the initial aqueous phase equilibrium state of the water in the MCL diagram:

Plot in the diagram lines representing the measured values for Alkalinity and pH of the raw water. Intersection of these lines occurs at Point 1 which establishes the initial aqueous phase equilibrium condition of the water. The initial Acidity is then the Acidity ordinate value of Point 1, i.e.

Acidity(initial) = 380 mg/ℓ as $CaCO_3$.

(iii) Establish the initial CO_2 saturation state with respect to the air:

For equilibrium between carbonate species in the aqueous phase and CO_2 in the air, the aqueous phase equilibrium point (given by any pair of values for pH, Alkalinity and Acidity) lies on Line A (see Section 4.4). In this example the initial aqueous phase equilibrium point lies underneath Line A so that given the opportunity the water will expel CO_2.

(iv) Determine new pH, Alkalinity and Acidity for equilibrium with CO_2 in the air:

Expulsion of CO_2 from the water causes Acidity to decrease, Alkalinity remains constant and pH increases. Thus, with CO_2 expulsion from the water the aqueous phase equilibrium point moves along the initial Alkalinity line until Line A is reached, i.e. Point 2. The new condition of the water is given by the Alkalinity, Acidity and pH values for

Point 2, i.e.

Alk(new) = Alk(initial) = 320 mg/ℓ
Acidity(new) = 300 mg/ℓ
pH(new) = 8,83.

Note that this new condition is established provided equilibrium is attained with CO_2 in the air, and, provided no $CaCO_3$ precipitation occurs during the CO_2 expulsion process.

(v) Determine the new $CaCO_3$ precipitation potential:

After CO_2 equilibrium is attained with the air the condition of the water will be Alkalinity 320 mg/ℓ, Ca^{2+} 210 mg/ℓ (both as $CaCO_3$) and pH 8,83 (provided that no $CaCO_3$ precipitation occurs). The water is now supersaturated with respect to $CaCO_3$. The $CaCO_3$ saturated state which the water would attain with time (provided no further CO_2 exchange occurs) is given by intersection of lines representing (Alk-Ca) and Acidity, i.e.

(Alk-Ca) = (320 - 210) = 110 mg/ℓ
Acidity = 300 mg/ℓ.

Lines representing the values for these two parameters intersect at Point 3. When $CaCO_3$ saturation is attained, the lines representing Alkalinity, Ca^{2+} and pH through Point 3 give the saturated values for these parameters, i.e.

Alk(sat) = 270 mg/ℓ
Ca^{2+}(sat) = 160 mg/ℓ
pH(sat) = 7,59.

The $CaCO_3$ precipitation potential is given by either of the changes in Alkalinity or Ca^{2+} between the initial and saturated conditions, i.e.

$$
\begin{aligned}
CaCO_3 \text{ precipitation potential} &= \text{Alk(initial)} - \text{Alk(sat)} \\
&= \text{Ca(initial)} - \text{Ca(sat)} \\
&= 210 - 160 = 50 \text{ mg/ℓ}.
\end{aligned}
$$

(vi) Determine the mass concentration of CO_2 exchanged with the air:

The mass concentration of CO_2 exchanged with the air is given by the change in Acidity between the initial and final conditions, i.e.

$$
\begin{aligned}
CO_2 \text{ expelled} &= \text{Acidity(initial)} - \text{Acidity(new)} \\
&= 380 - 300 = 80 \text{ mg/ℓ as } CaCO_3.
\end{aligned}
$$

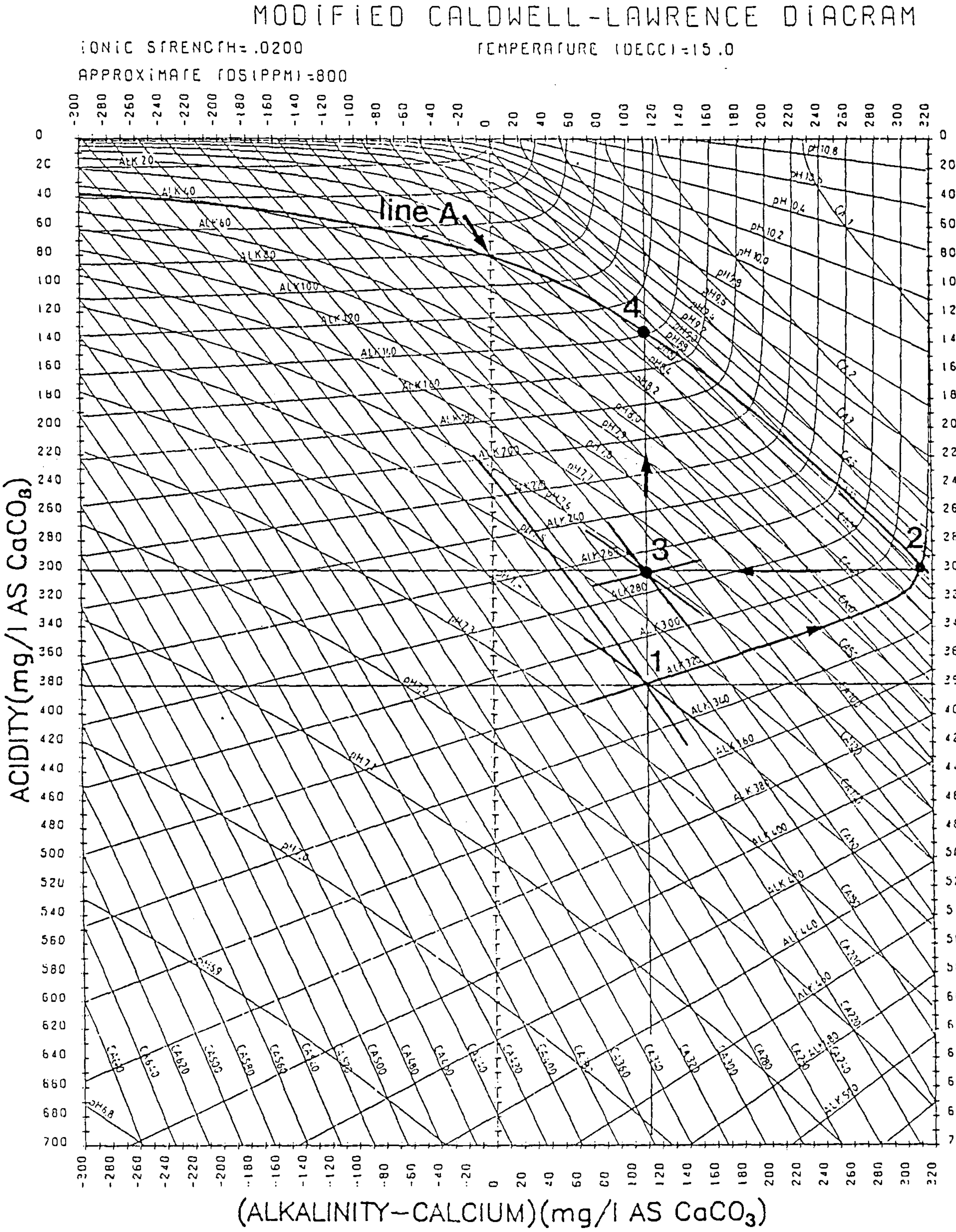


Fig 5.14 Example 12: CO_2 expulsion from water pumped to surface causes a $CaCO_3$ precipitation potential.

(b) Slow Co_2 exchange with association $CaCO_3$ precipitation:

In (a) above it was shown that CO_2 exchange with the air causes $CaCO_3$ supersaturation. Further, in that example if $CaCO_3$ precipitation was allowed after isolating the water from the air, eventually a $CaCO_3$ saturated condition was attained, depicted by Point 3 in Fig 5.14. After precipitation the aqueous CO_2 is no longer in equilibrium with CO_2 in the air, and, if exposed to the air the water again would expel CO_2 causing further $CaCO_3$ precipitation. Proceeding in this fashion, eventually a condition is attained where the water is both in equilibrium with CO_2 in the air (the state will be on Line A) and in equilibrium with solid $CaCO_3$ (a condition of three phase equilibrium, equilibrium between carbonate species in the aqueous, gaseous and solid phases.) This three phase equilibrium point therefore occurs vertically above Point 1 on the CO_2 equilibrium line, Line A, i.e. Point 4.

The $CaCO_3$ precipitation potential and the CO_2 exchange potential are determined in the following steps:

(i) Three phase equilibrium state point:

Values for Alkalinity, Ca^{2+} and pH at three phase equilibrium are given by the values for the lines for these parameters through Point 4, i.e.

Alk(3 phase) = 140 mg/ℓ
Ca^{2+}(3 phase) = 30 mg/ℓ.
pH = 8,52

(ii) Determine the $CaCO_3$ precipitation potential:

The $CaCO_3$ precipitation potential is given by either of the changes in Alkalinity or Ca^{2+} between the initial and saturated three phase condition, i.e.

$CaCO_3$ precipitation potential = Alk(initial) - Alk(3 phase)
= 320 - 140 = 180 mg/ℓ,
i.e. 180 kg $CaCO_3$ per Mℓ.

(iii) Determine the mass concentration of CO_2 exchanged with the air:

The mass concentration of CO_2 exchanged with the air is given by the change in Acidity between the initial and the final three phase condition (i.e. Point 4). The final Acidity is determined from the Acidity ordinate value of Point 4, i.e.

Acidity(3 phase) = 135 mg/ℓ
and
CO_2 expelled = Acidity(initial) - Acidity(3 phase)
= 380 - 135
= 245 mg/ℓ as $CaCO_3$.
i.e. 245 kg CO_2 (as $CaCO_3$)/Mℓ

REFERENCES

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Kunin R (1972) Water softening by ion exchange, Proc Fourteenth Water Quality Conf. University of Illinois, IL.

Loewenthal R E and Marais G v R (1976) Carbonate Chemistry of Aquatic Systems: Theory and Application, Ann Arbor Sci Publ., Ann Arbor.

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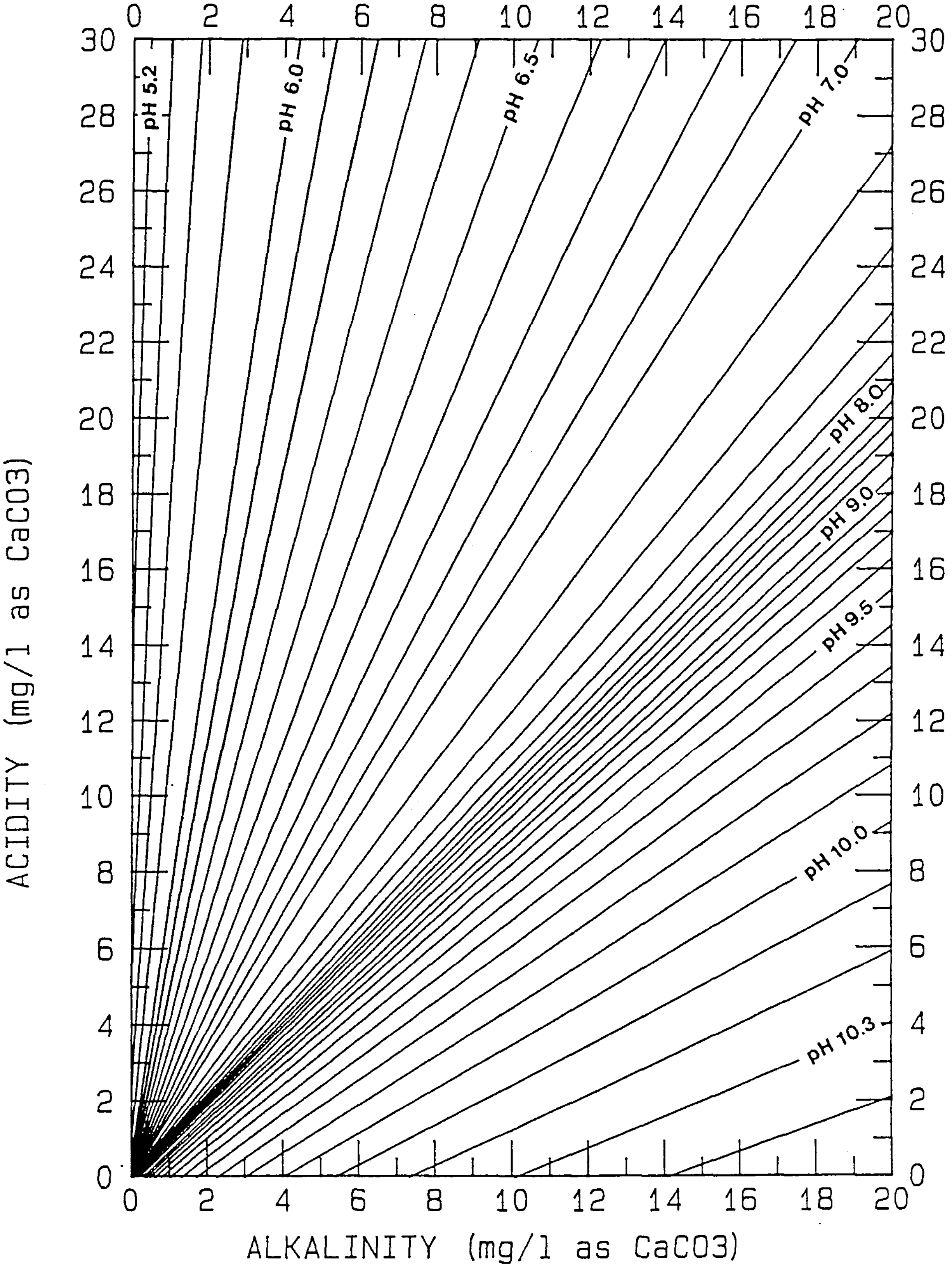
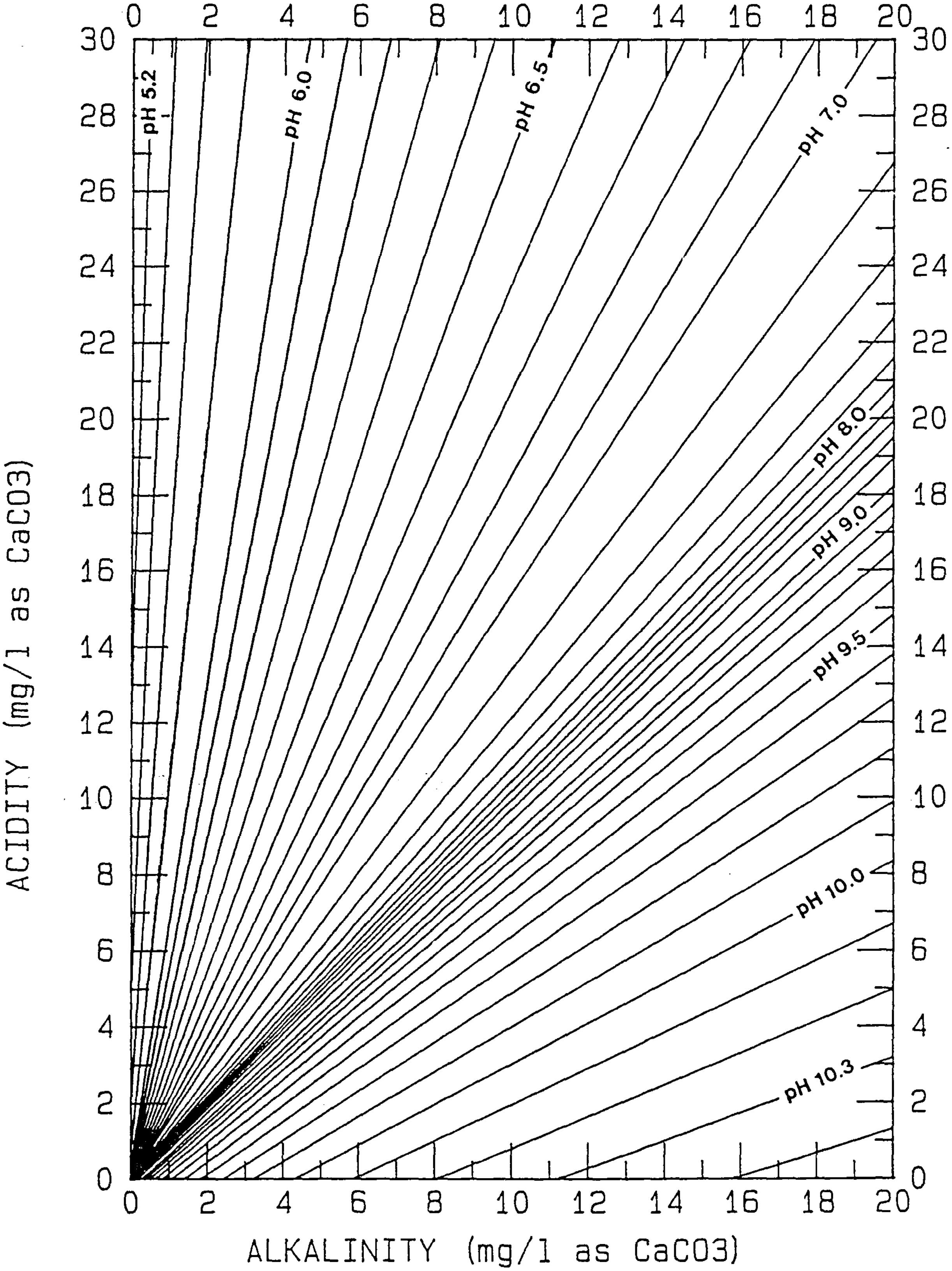
APPENDIX A

DEFFEYES TYPE SINGLE PHASE CONDITIONING DIAGRAMS

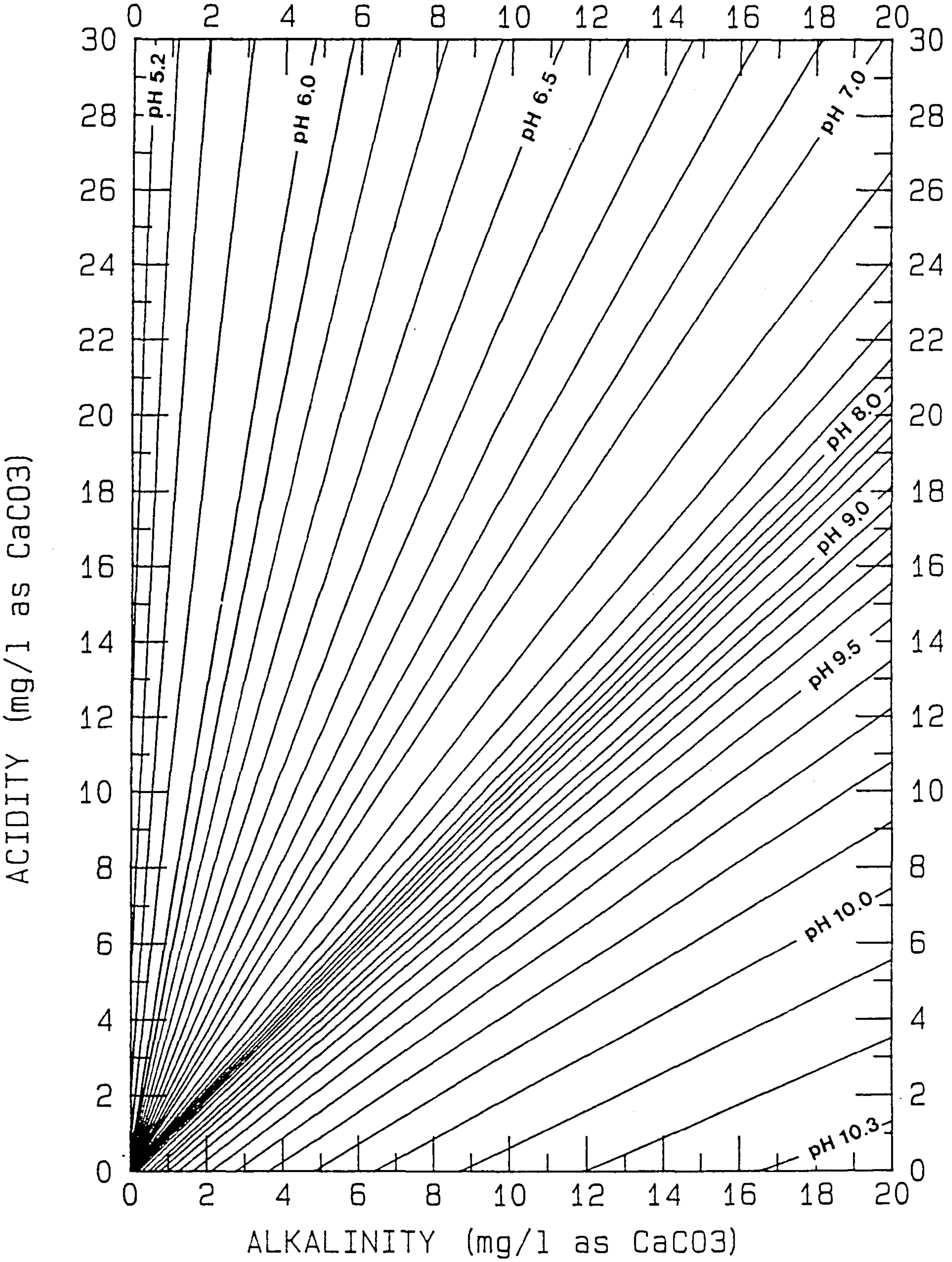
IONIC STRENGTH=0.001 (TDS= 40mg/l)
TEMPERATURE (DEGC) = 10



IONIC STRENGTH=0.010 (TDS=400mg/l)
TEMPERATURE (DEGC) = 10



IONIC STRENGTH=0.001 (TDS= 40mg/l)
TEMPERATURE (DEGC) = 15



IONIC STRENGTH=0.010 (TDS=400mg/l)
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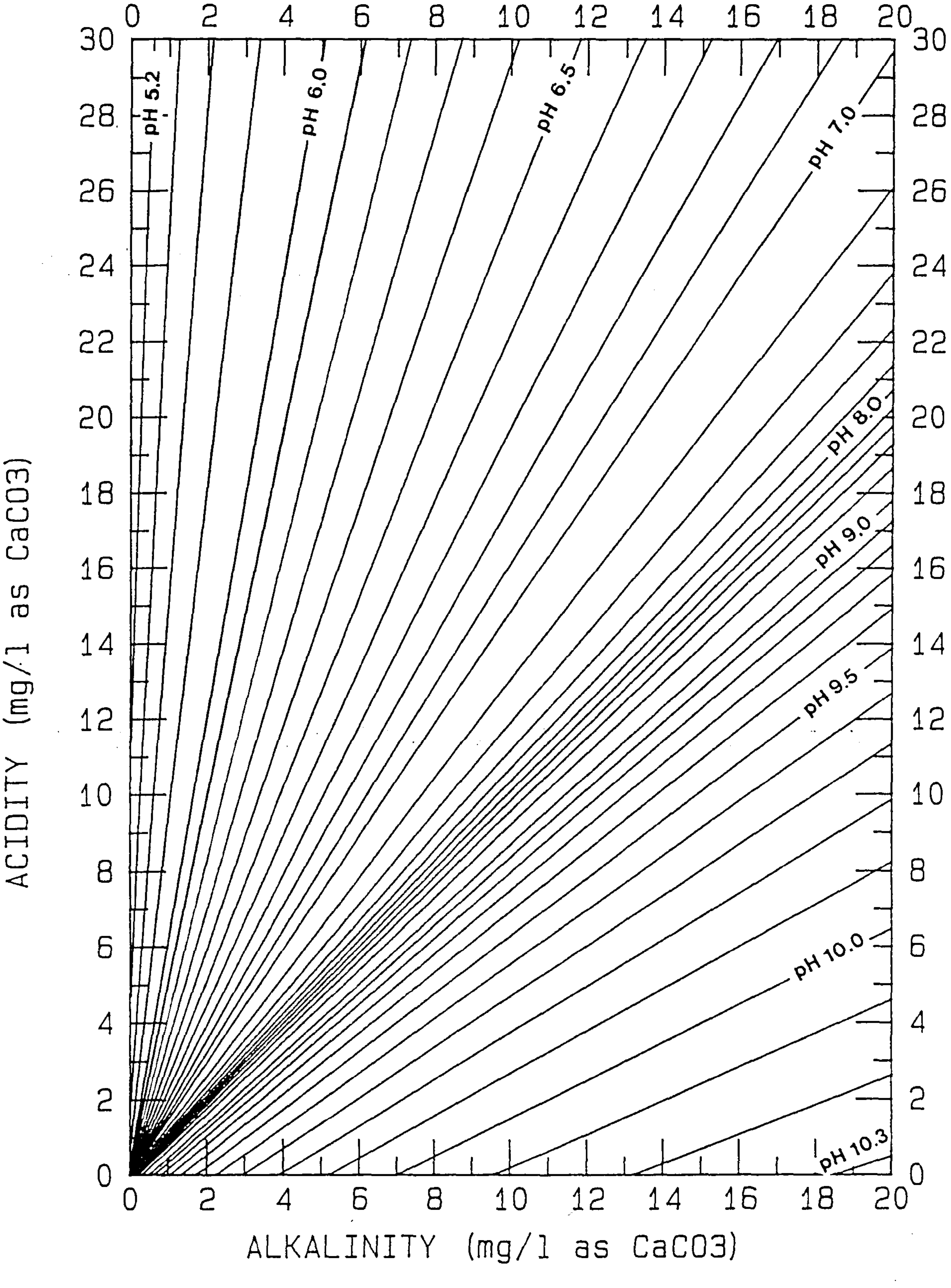
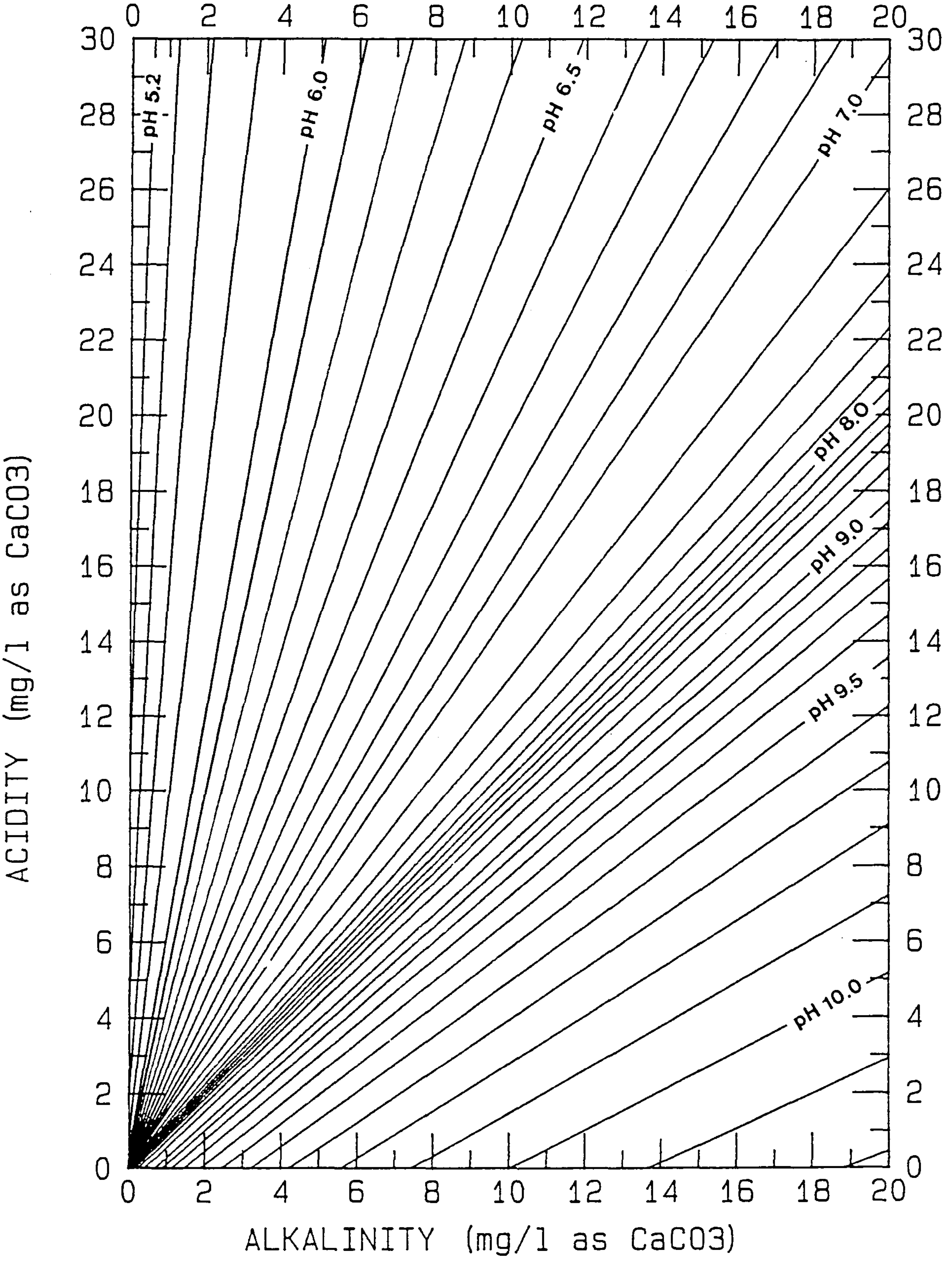
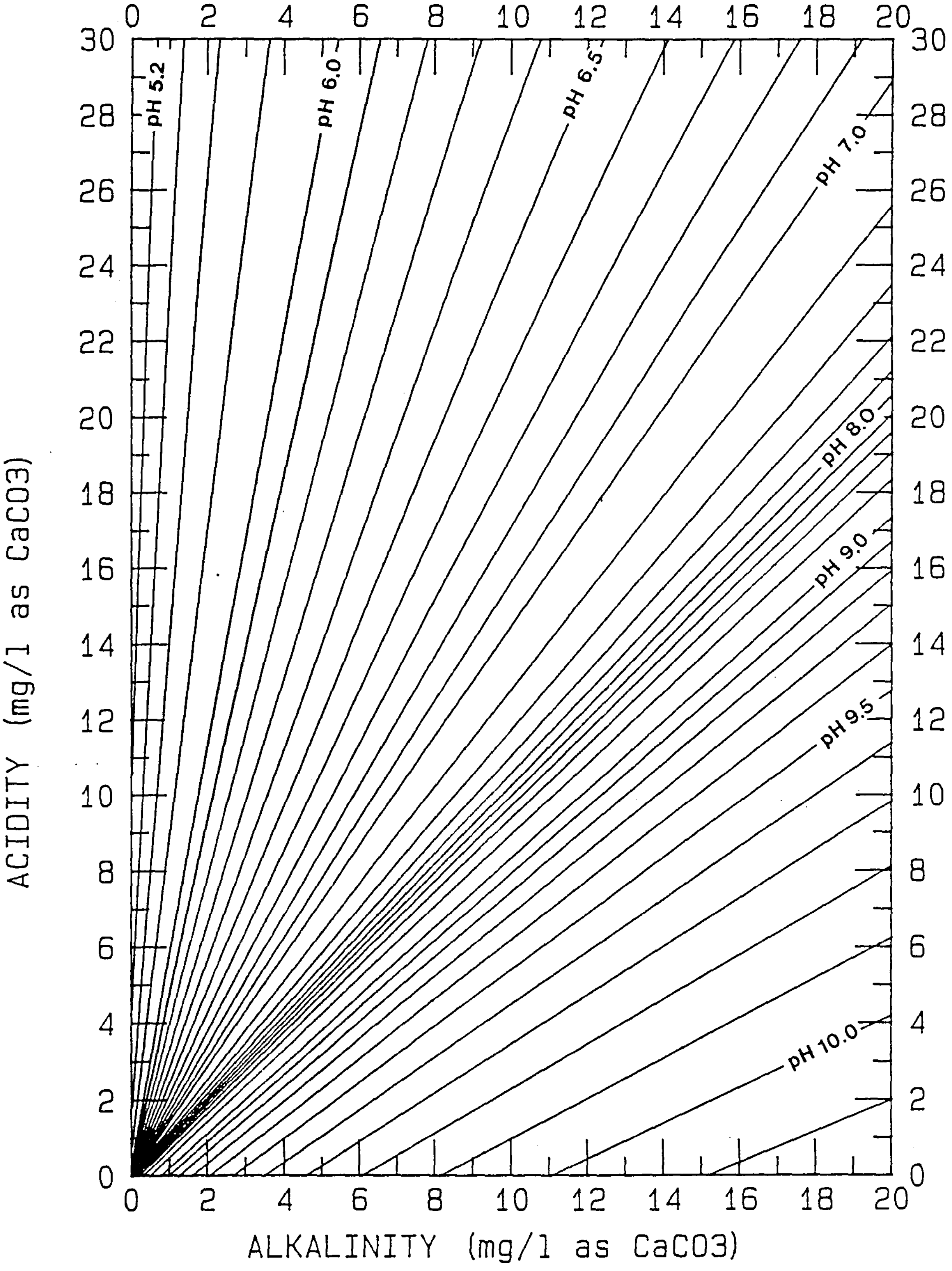


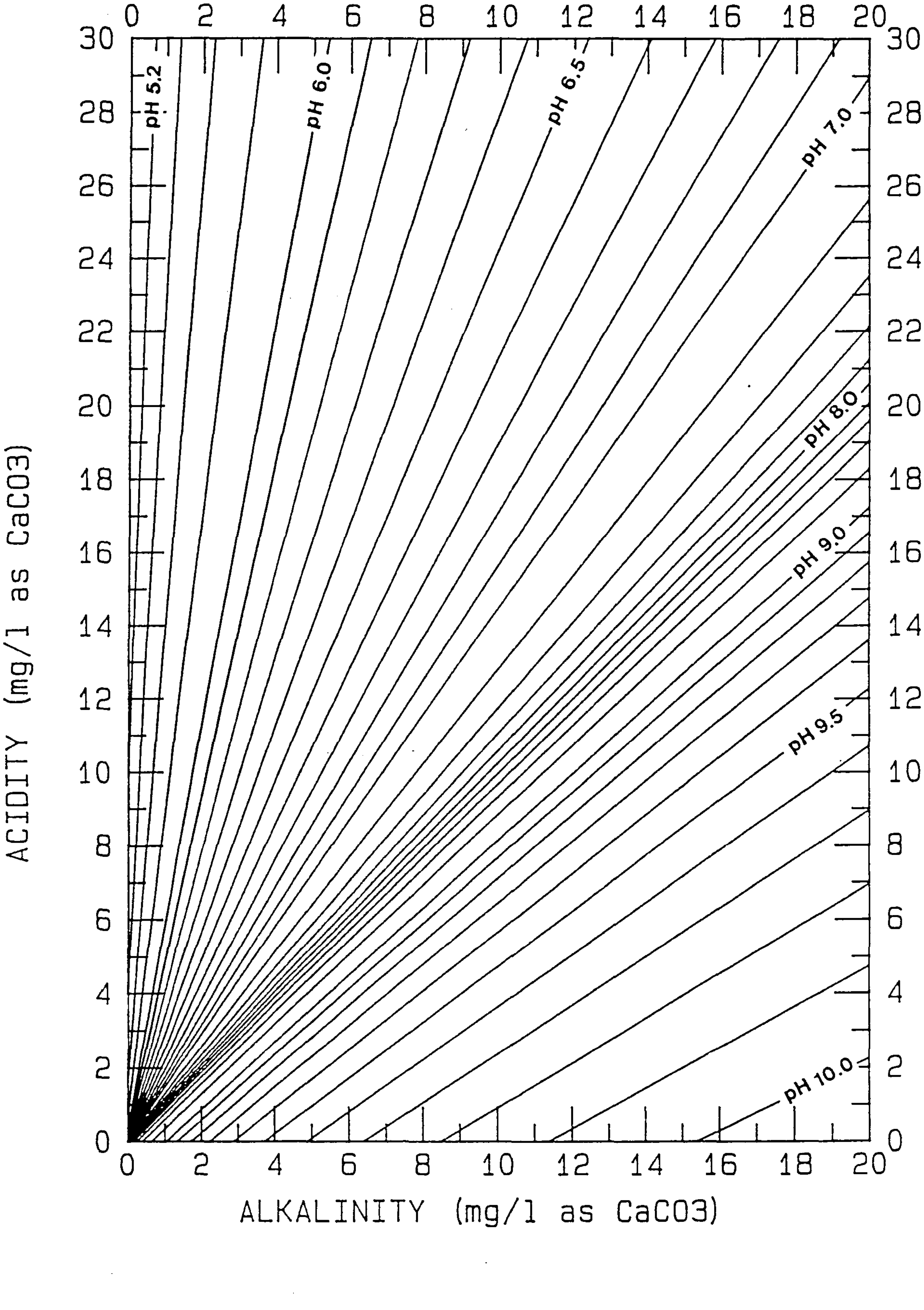
IONIC STRENGTH=0.001 (TDS= 40mg/l)
TEMPERATURE (DEGC) = 20



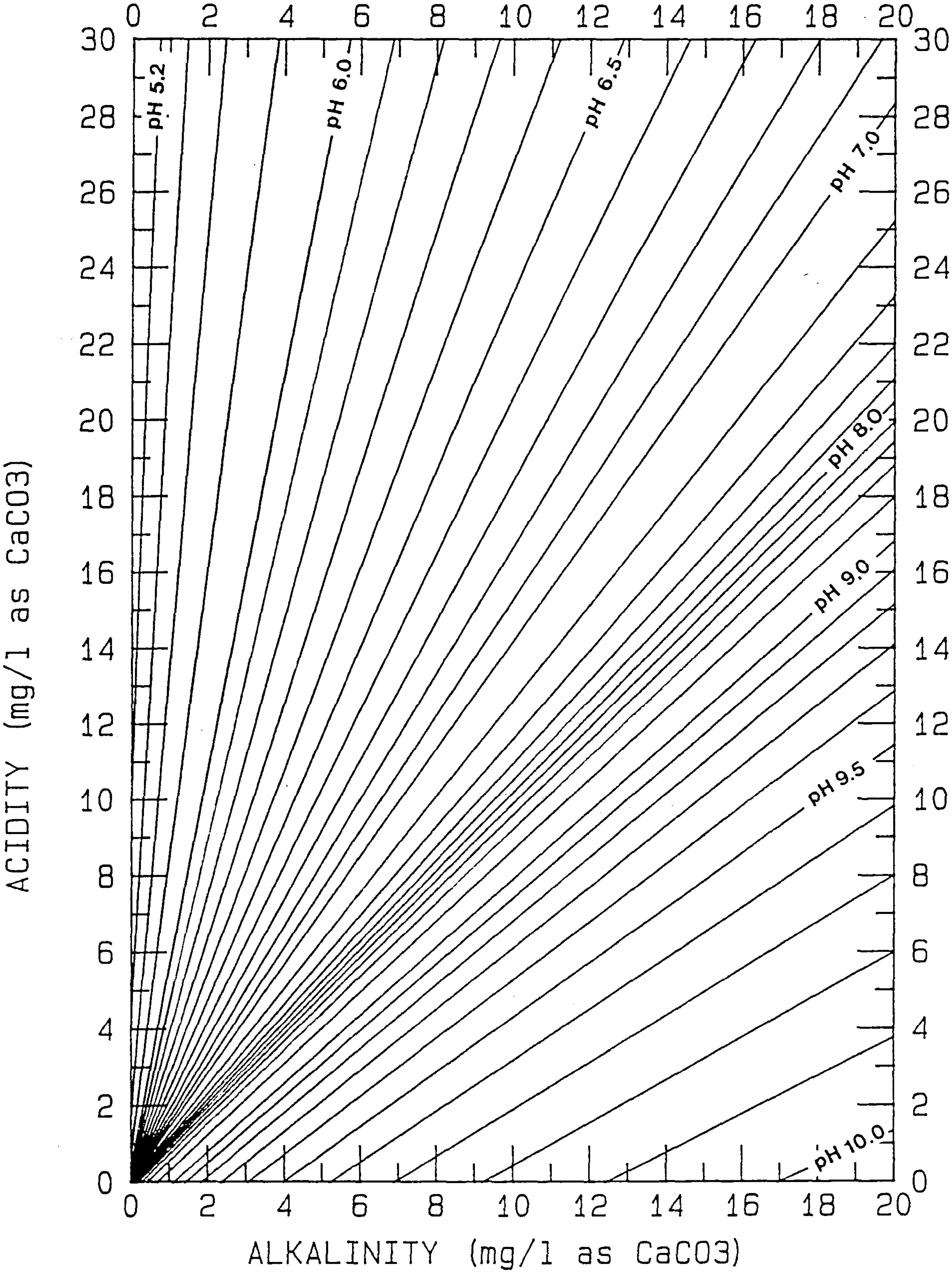
IONIC STRENGTH=0.010 (TDS=400mg/l)
TEMPERATURE (DEGC) = 20



IONIC STRENGTH=0.001 (TDS= 40mg/l)
TEMPERATURE (DEGC) = 25



IONIC STRENGTH=0.010 (TDS=400mg/l)
TEMPERATURE (DEGC) = 25



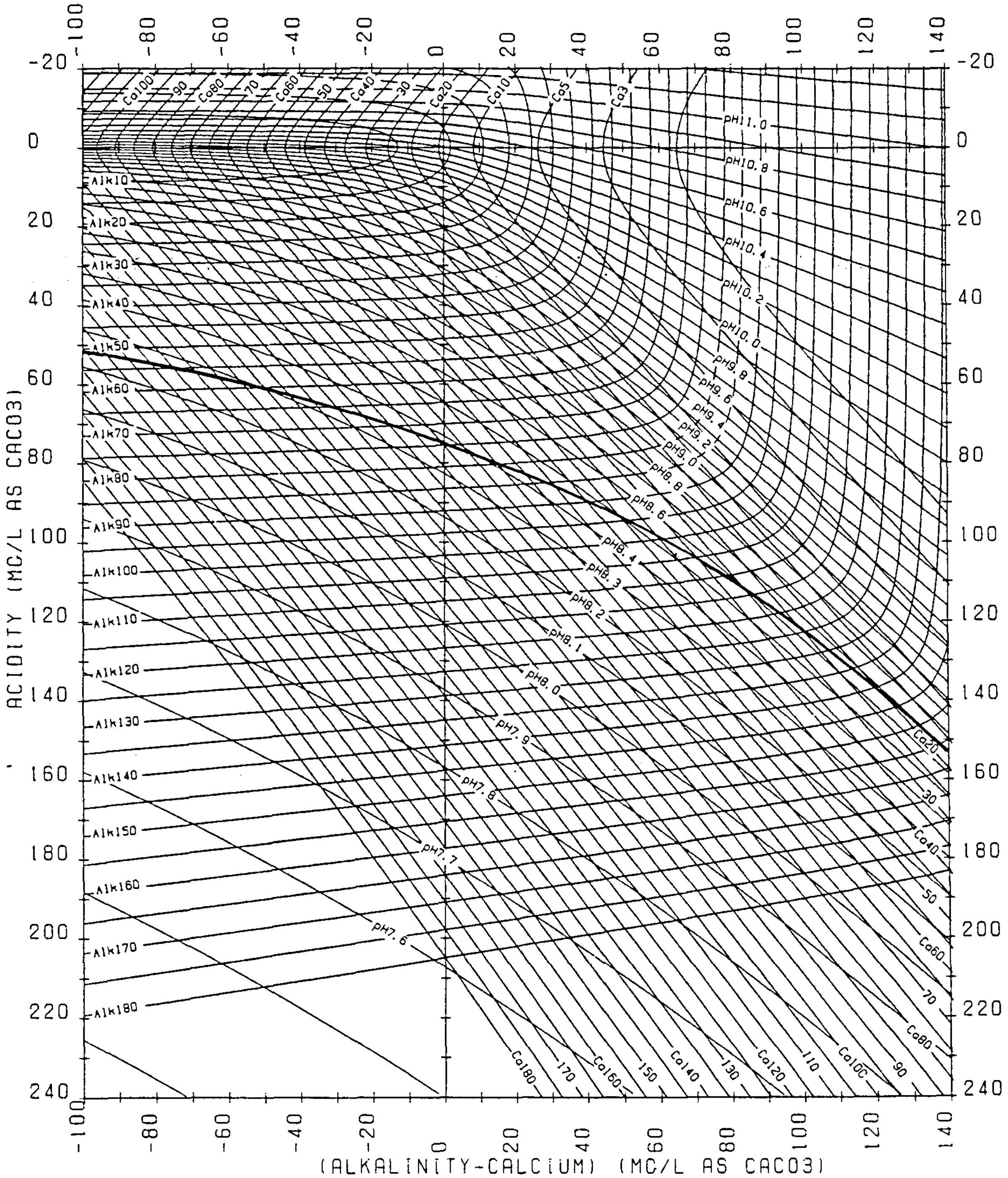
APPENDIX B

MODIFIED CALDWELL-LAWRENCE CONDITIONING DIAGRAMS

MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0010 TEMPERATURE (DEGC)=10.0

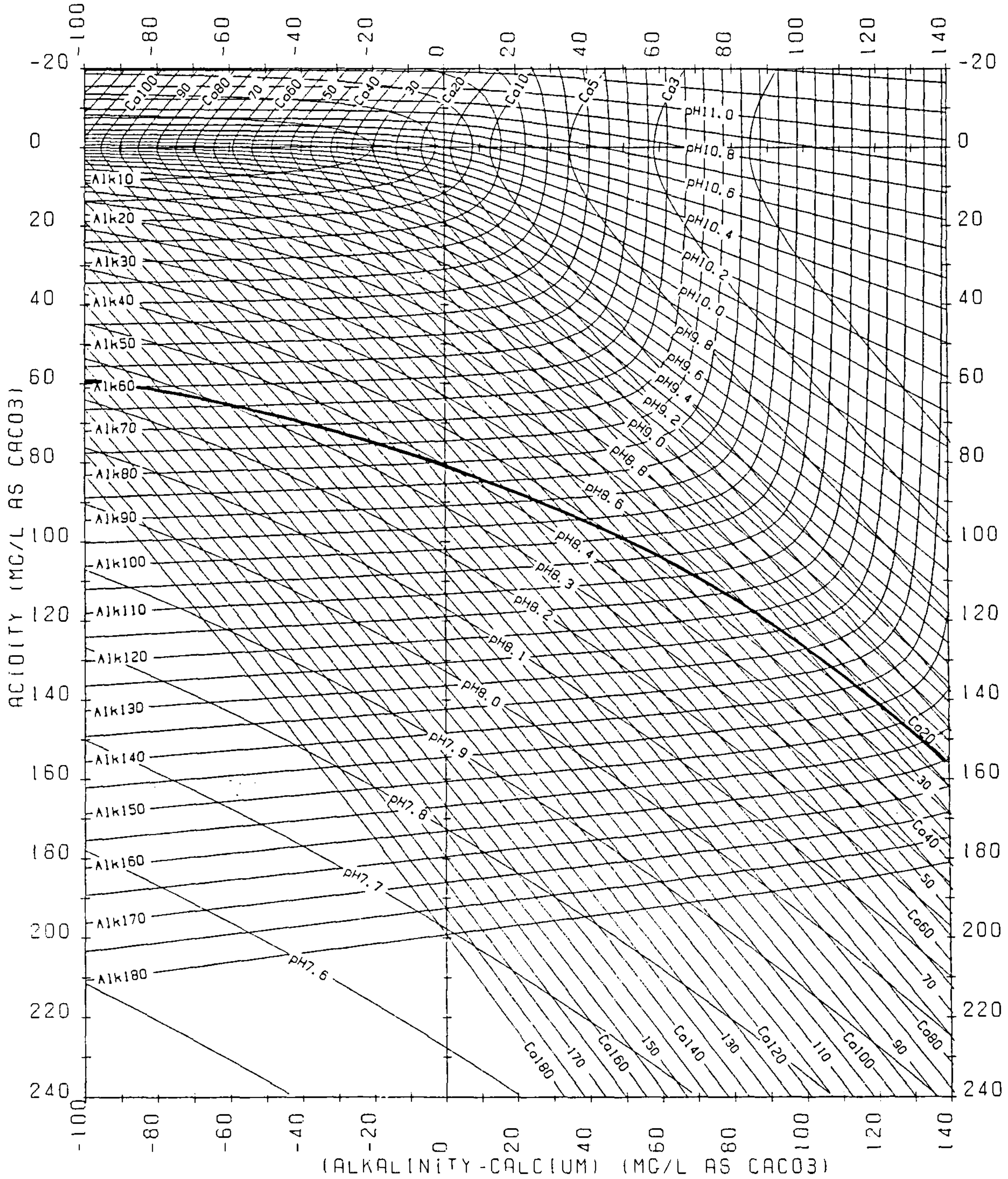
APPROXIMATE TDS(MG/L)=40



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0050 TEMPERATURE (DEGC)=10.0

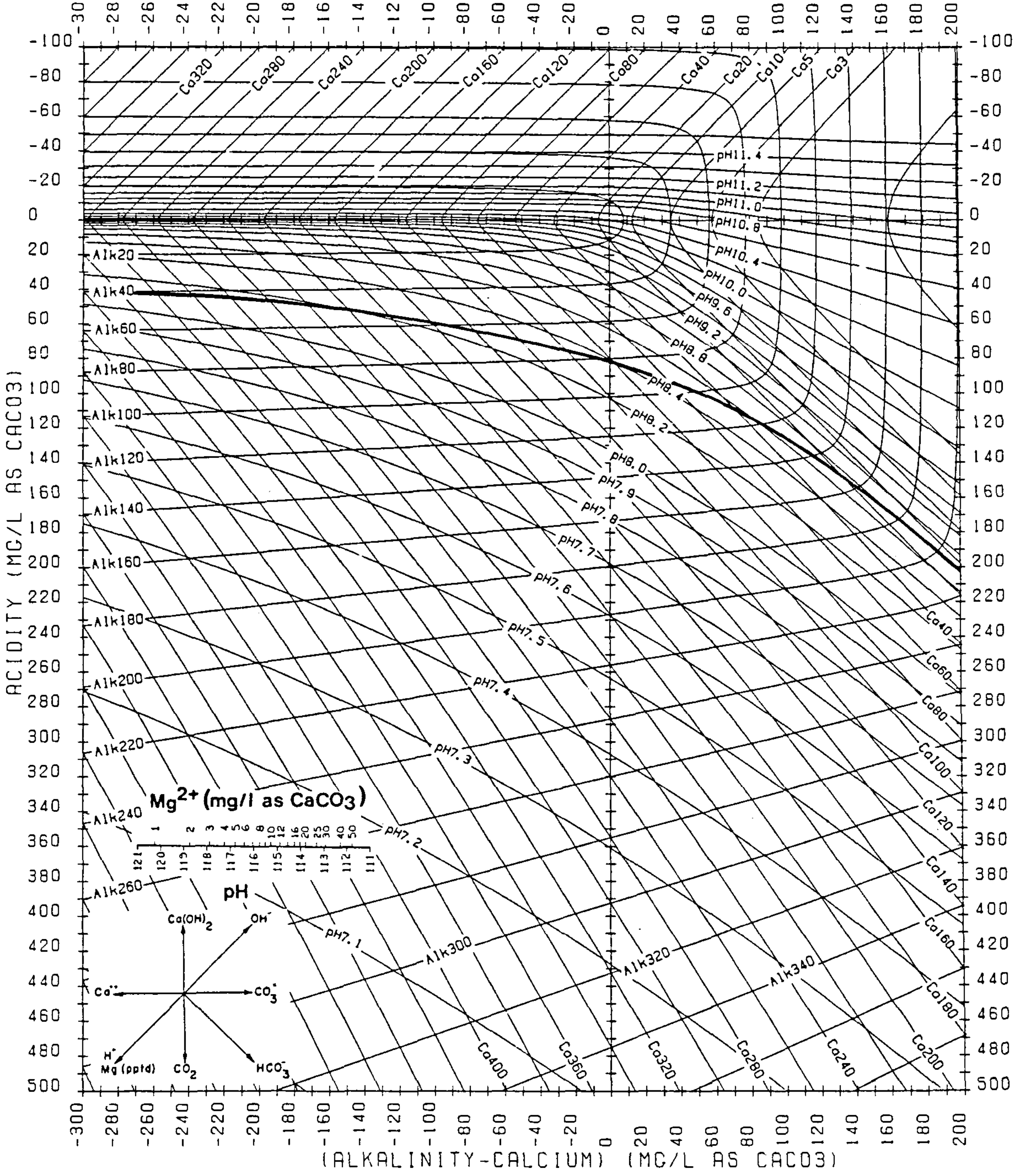
APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0050 TEMPERATURE (DEGC)=10.0

APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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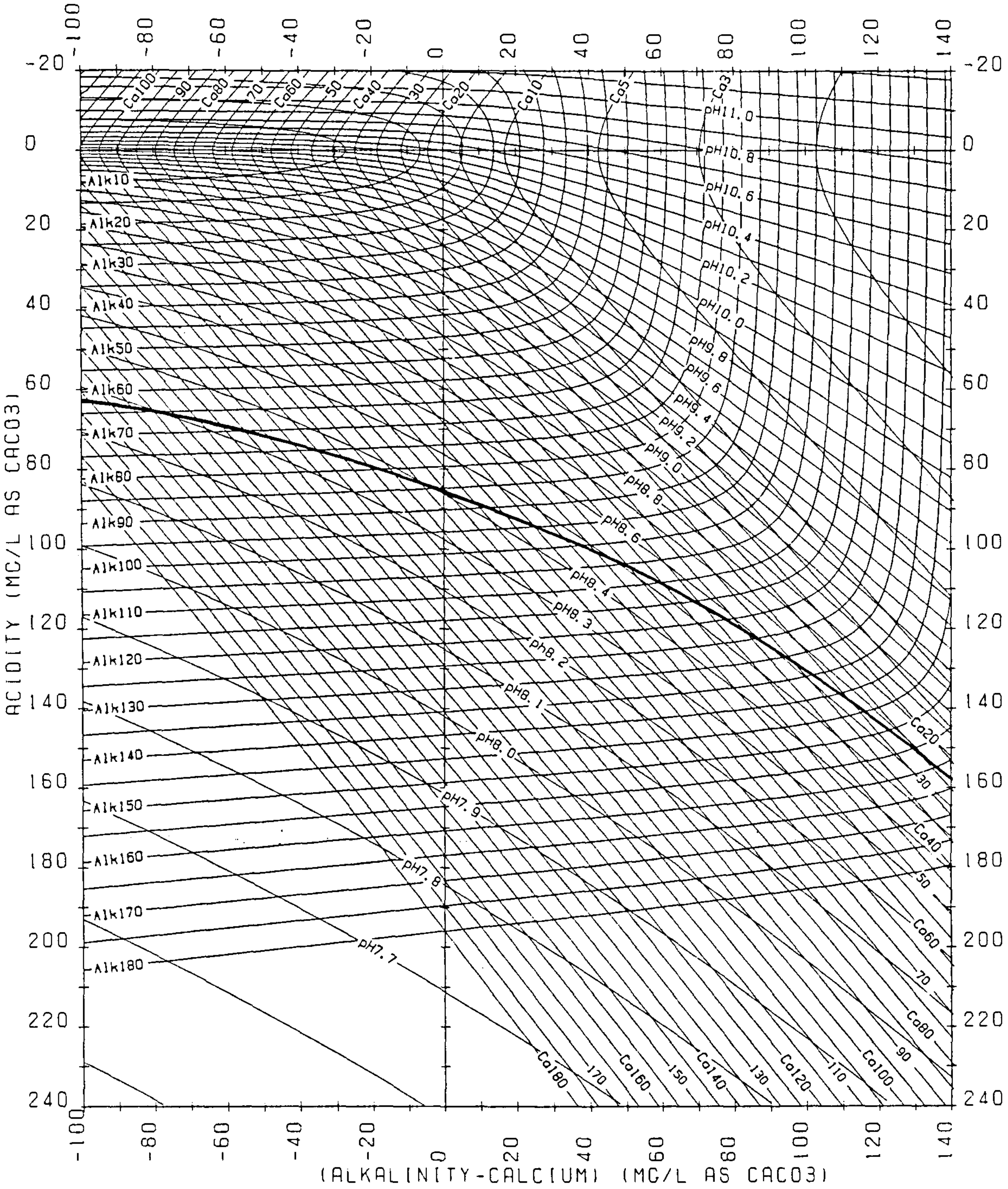
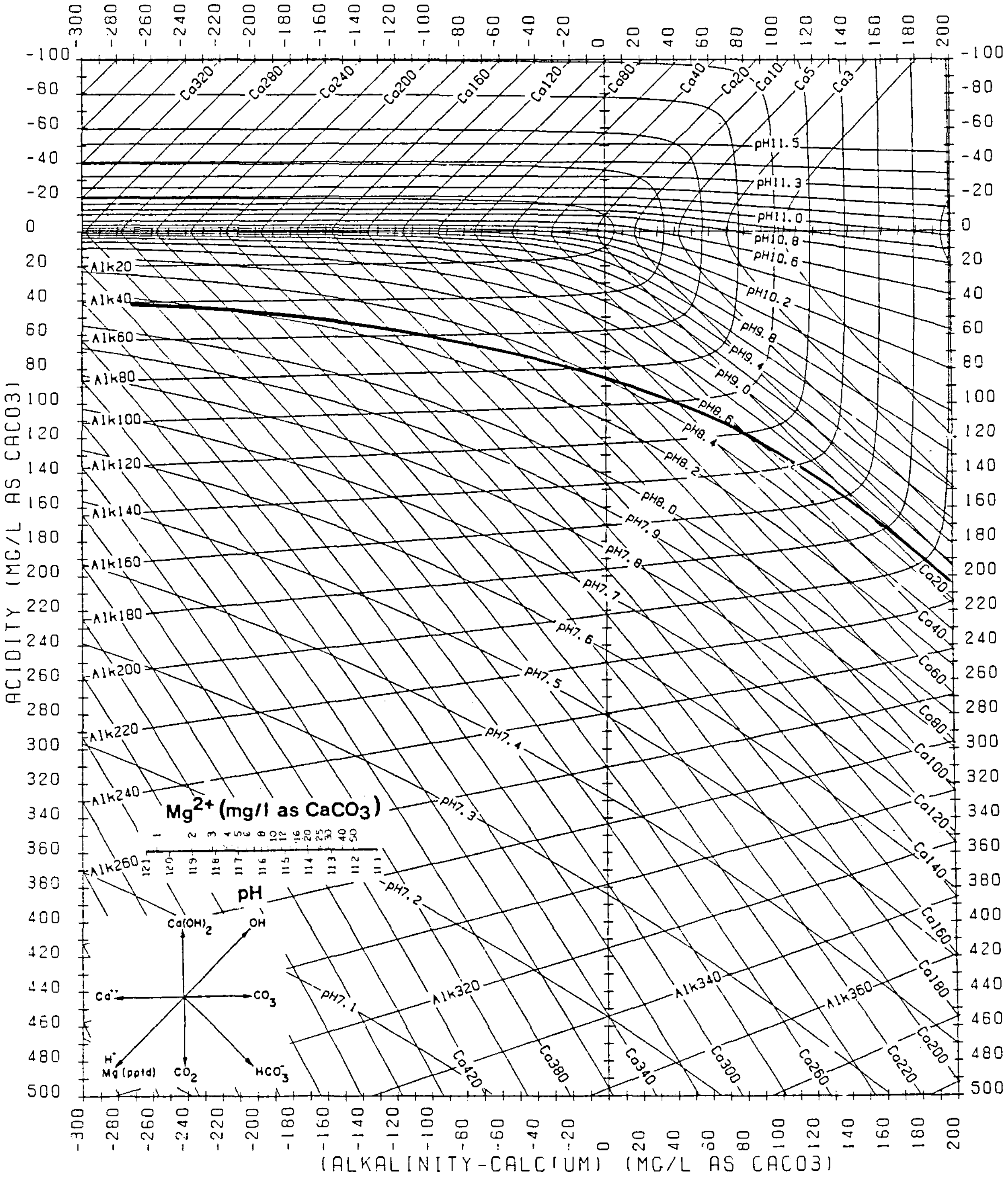
APPROXIMATE TDS(MG/L)=400



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH=.0100 TEMPERATURE (DEGC)=10.0

APPROXIMATE TDS(MG/L)=400



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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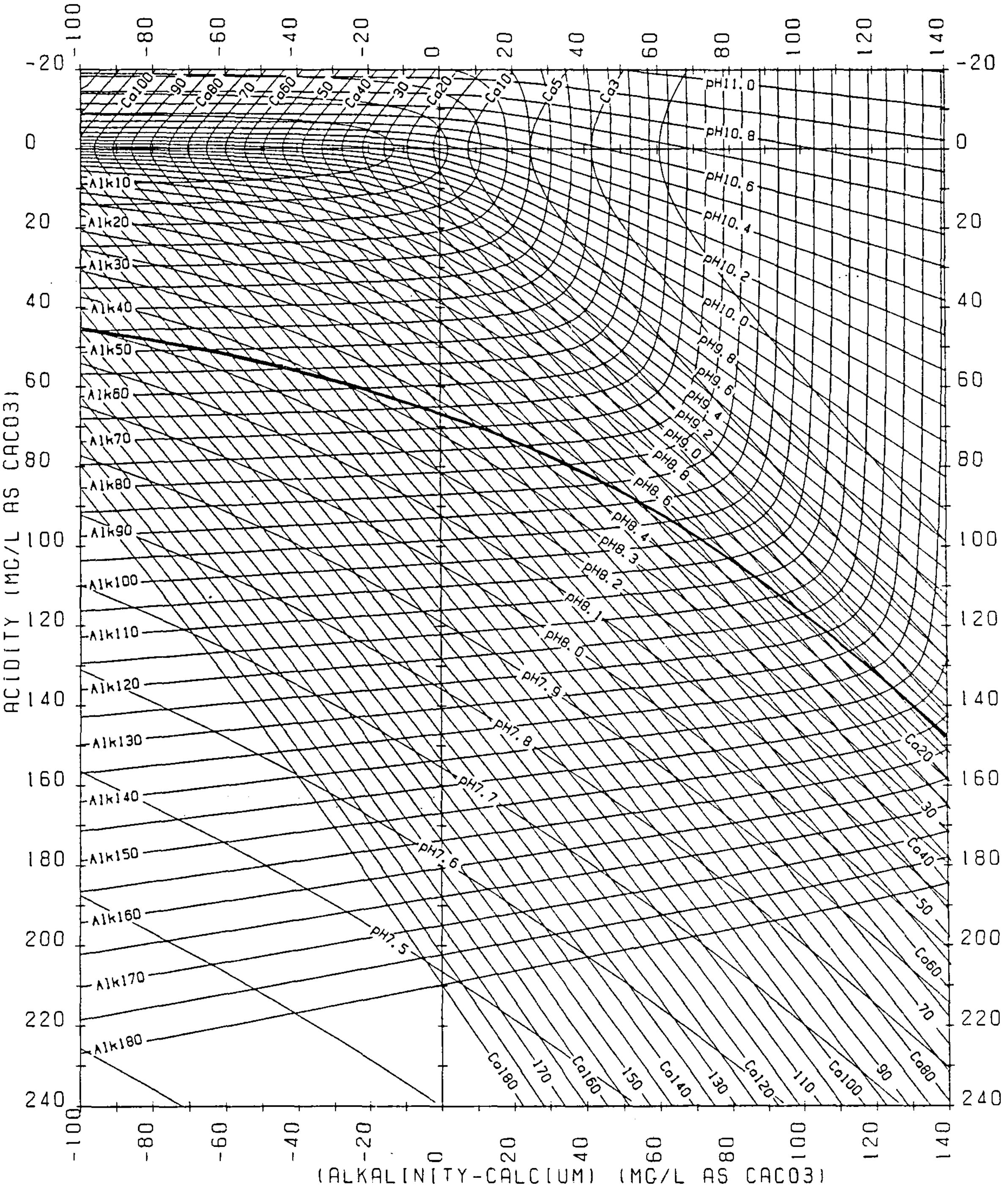

MODIFIED CALDWELL-LAWRENCE DIAGRAM

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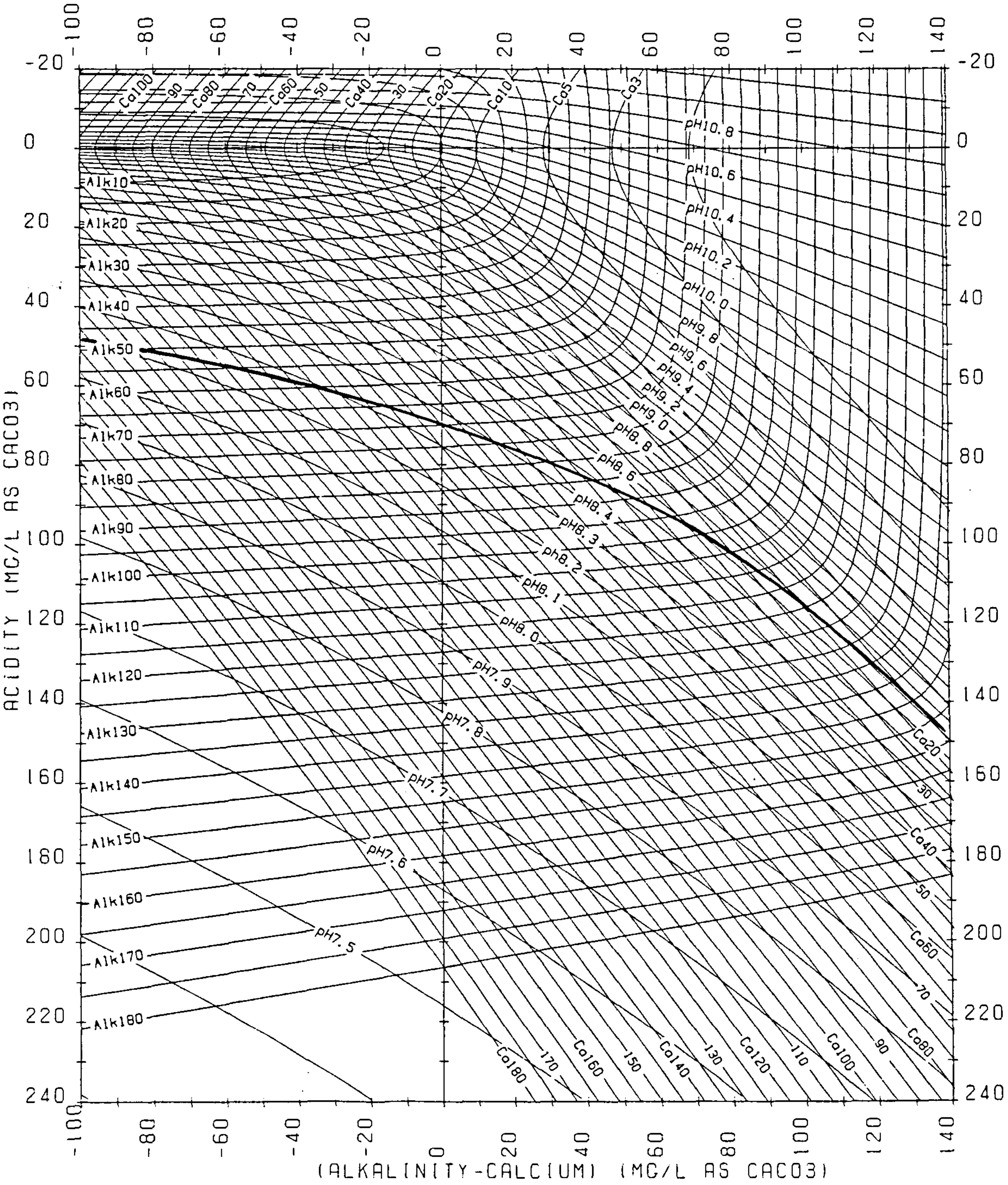
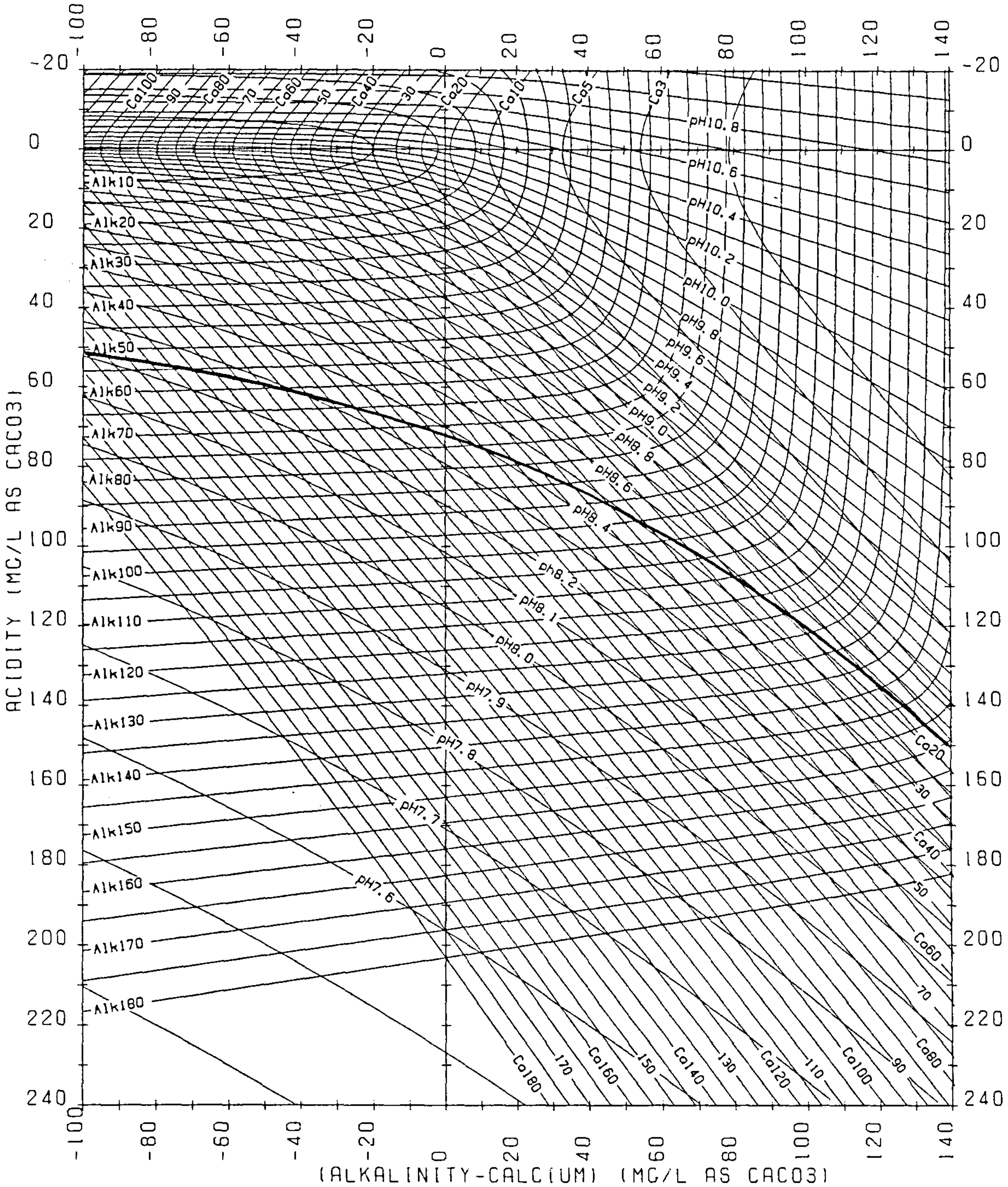
APPROXIMATE TDS(MG/L)=100



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0050 TEMPERATURE (DEGC)=15.0

APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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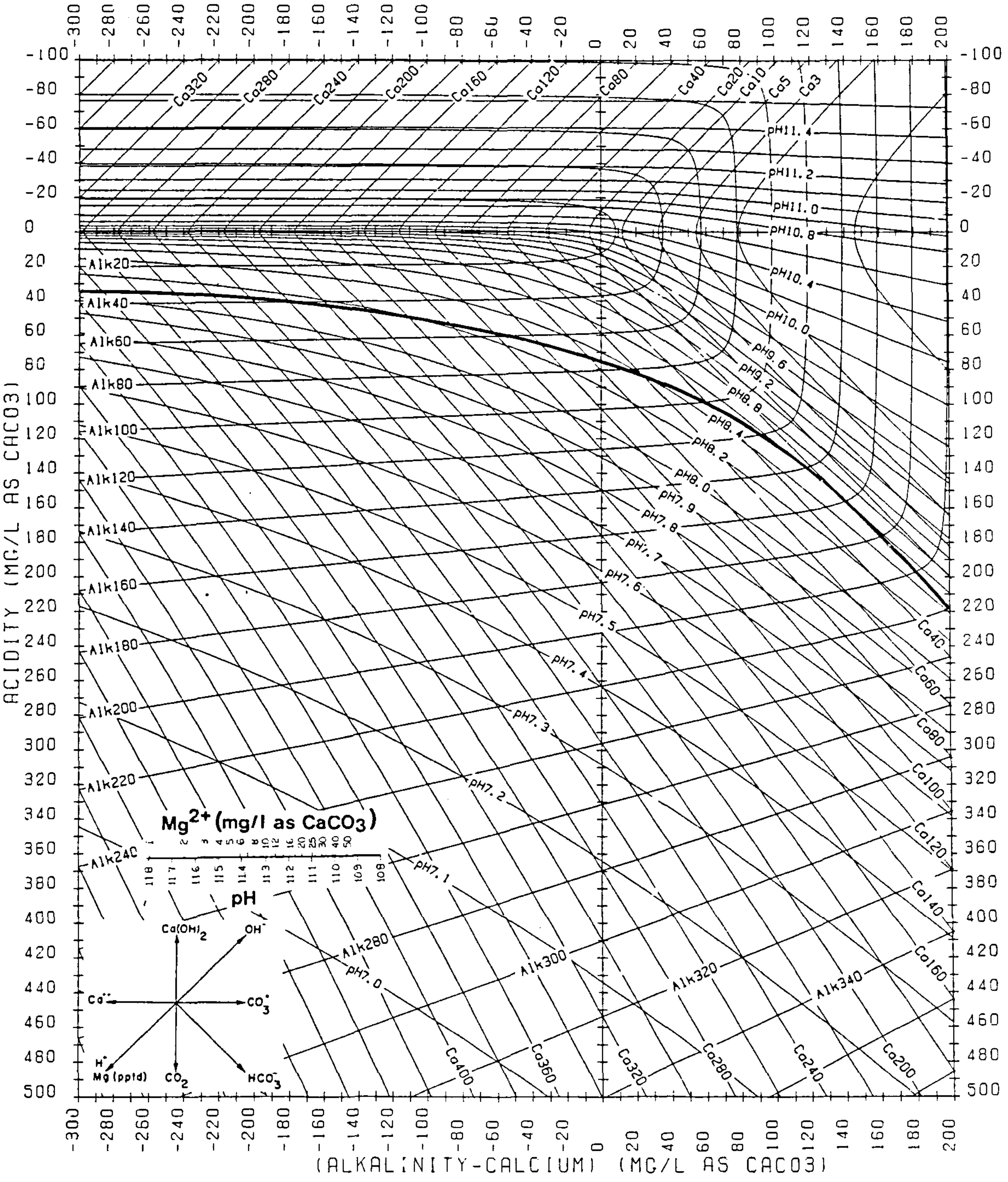
APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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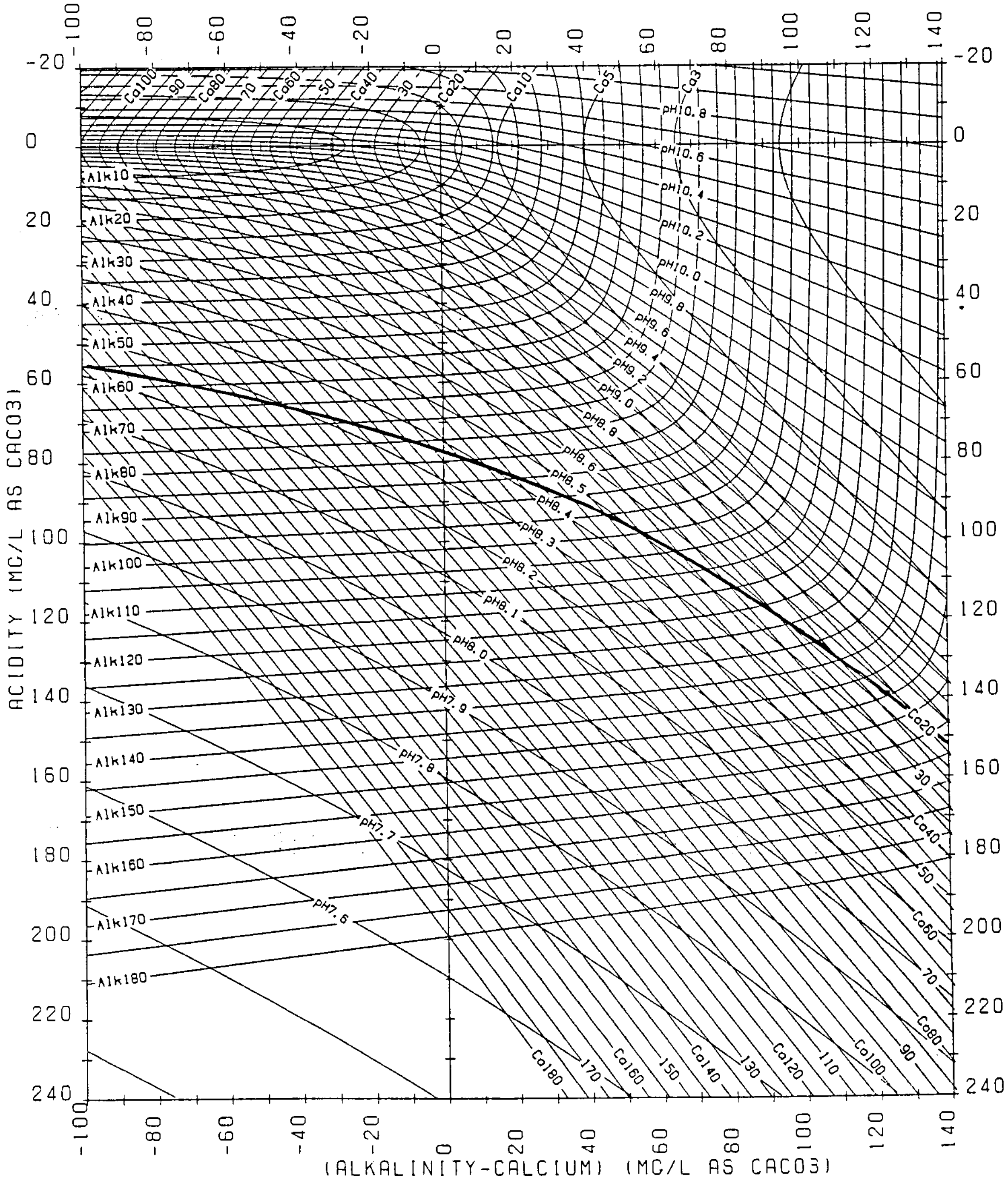
APPROXIMATE TDS(MG/L)=400



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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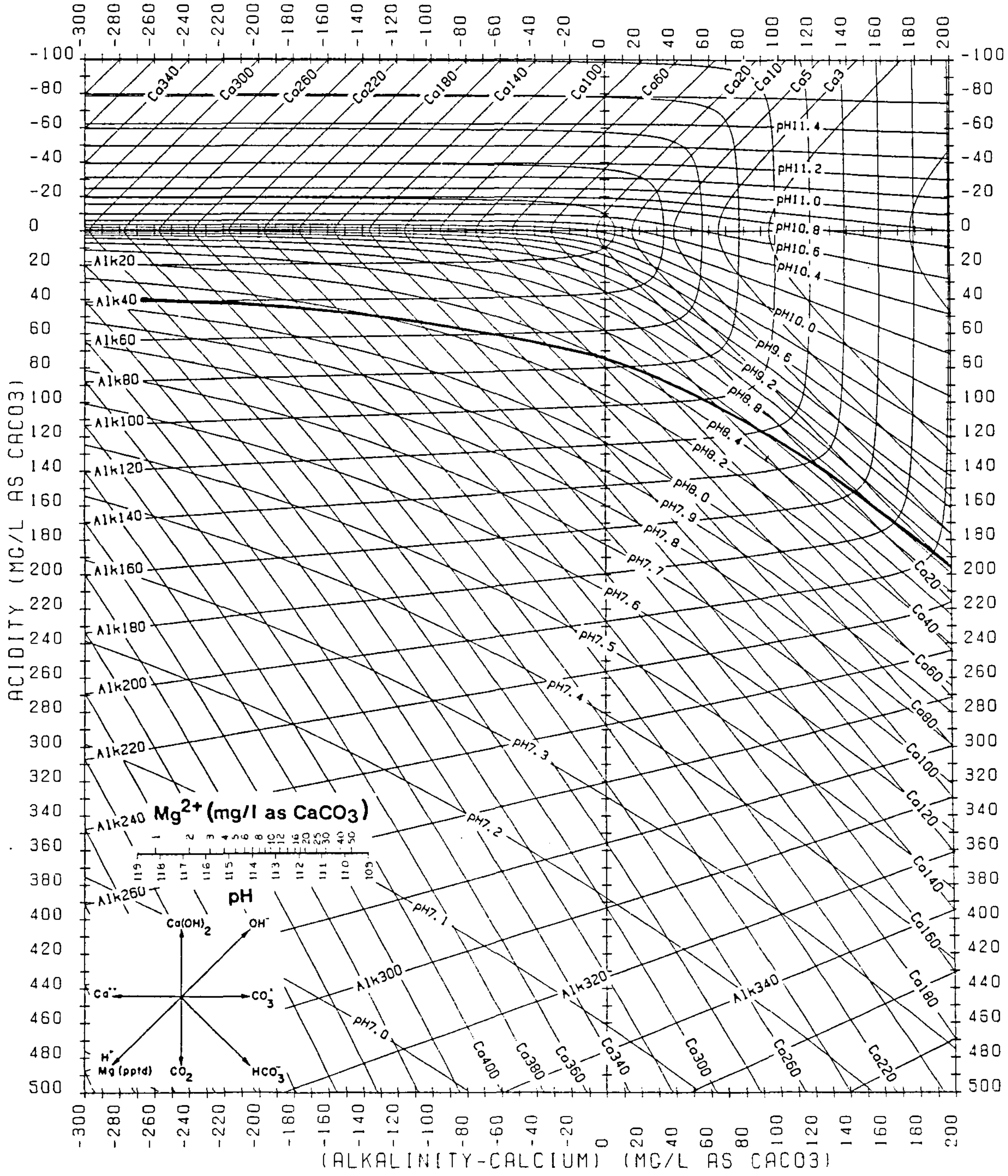
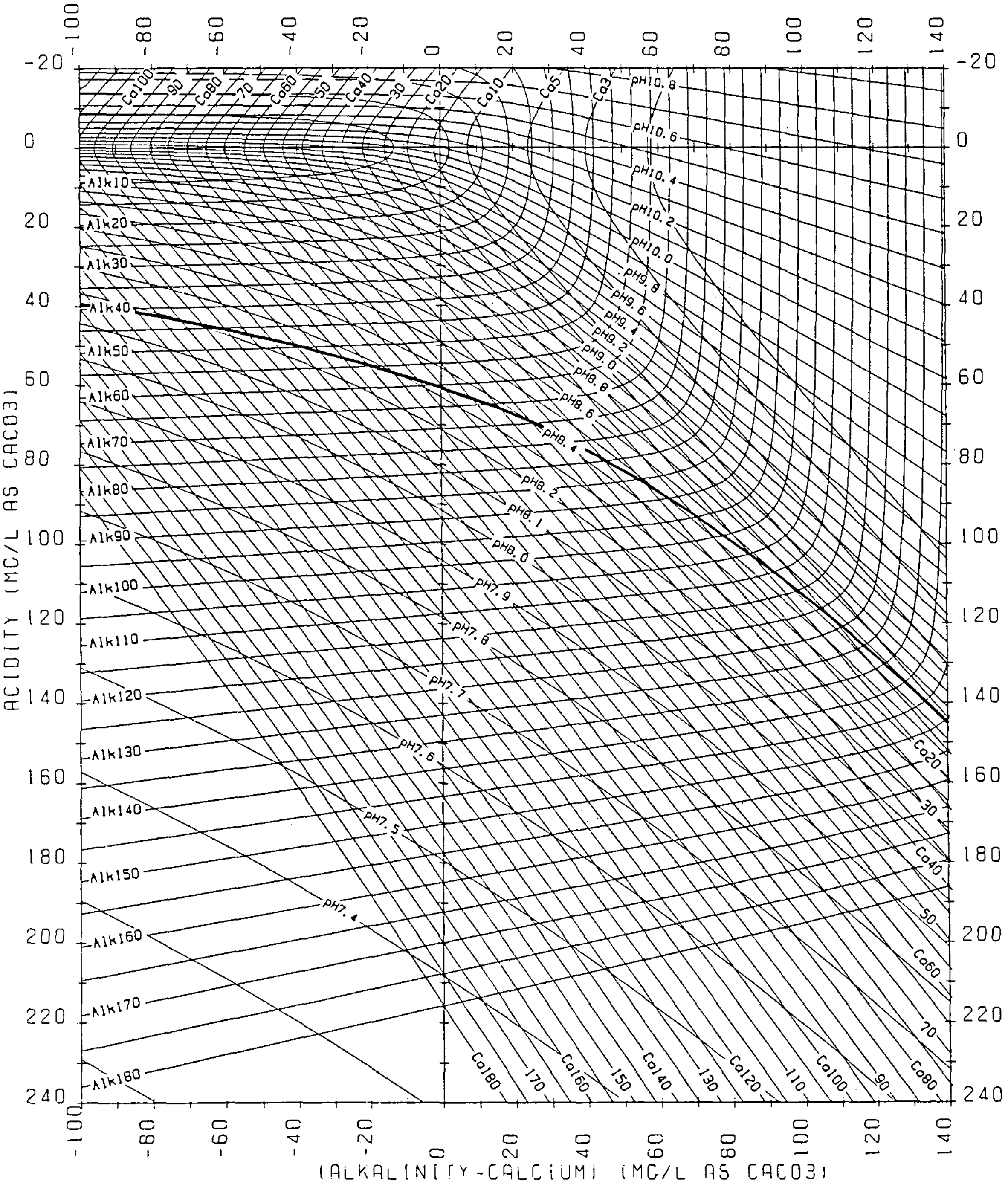
APPROXIMATE TDS(MG/L)=400



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0010   TEMPERATURE (DEGC)=20.0

APPROXIMATE TDS(MG/L)=40



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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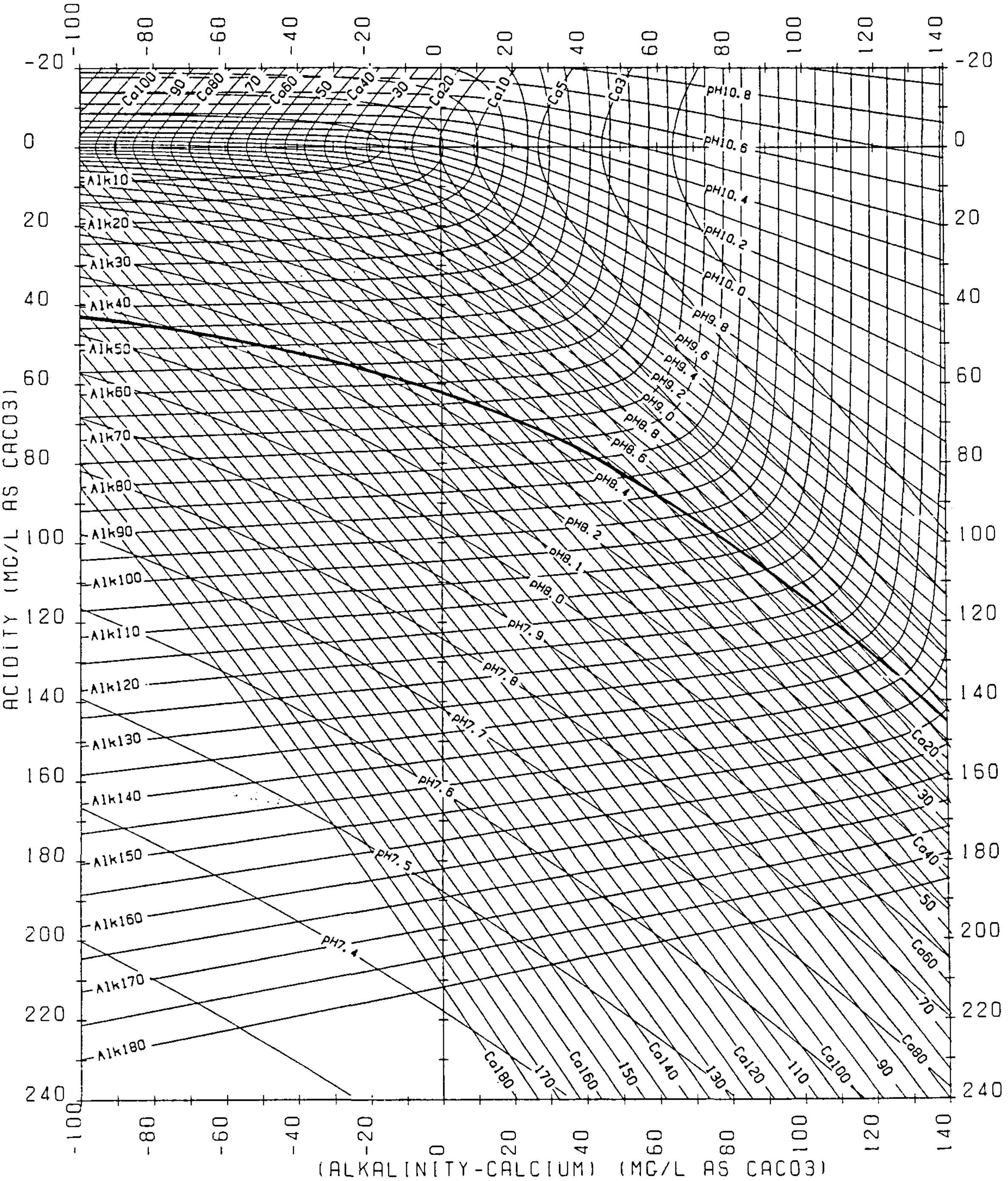
APPROXIMATE TDS(MG/L)=100



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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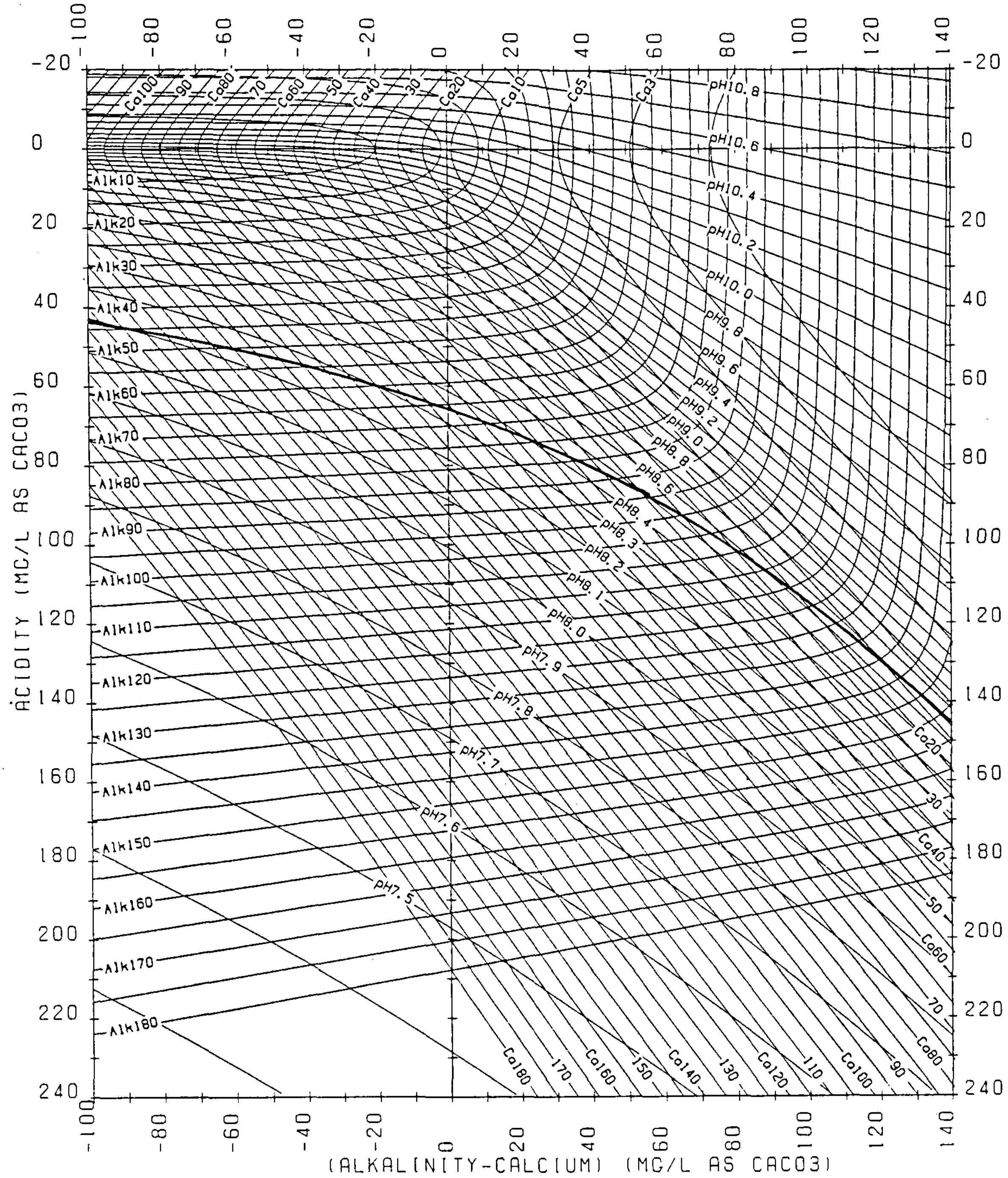
APPROXIMATE TDS(MG/L)=200



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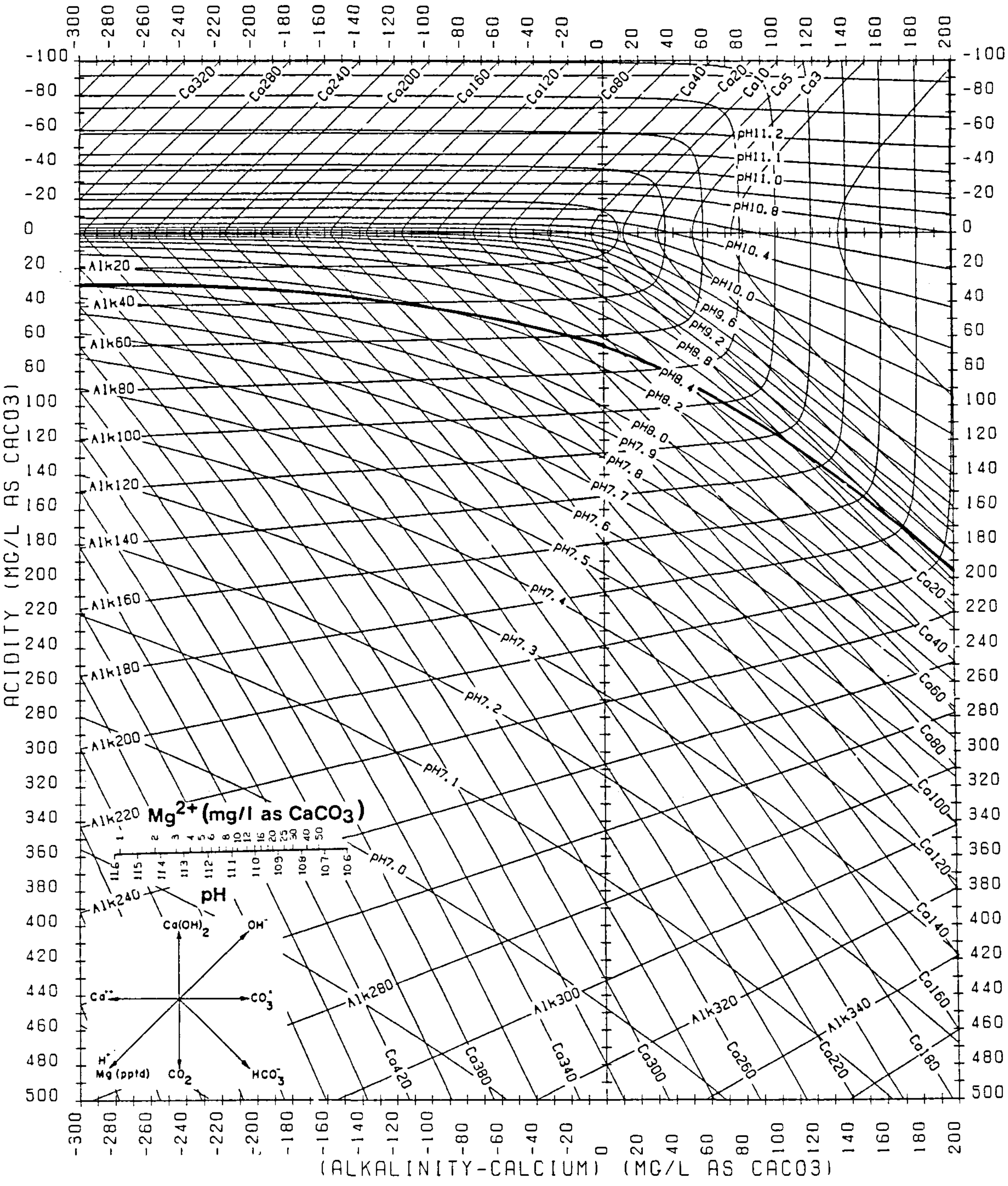

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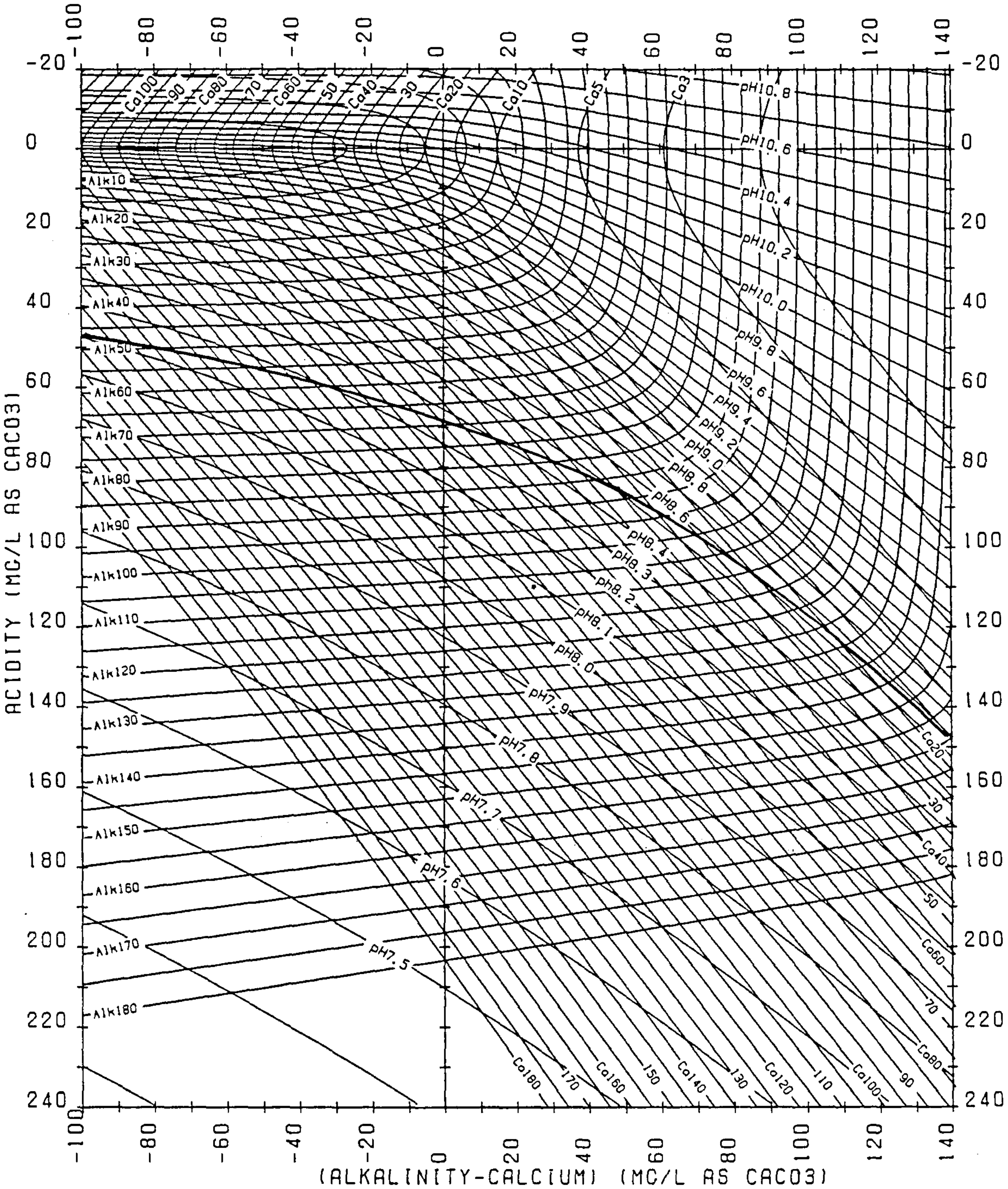
APPROXIMATE TDS(MG/L)=400



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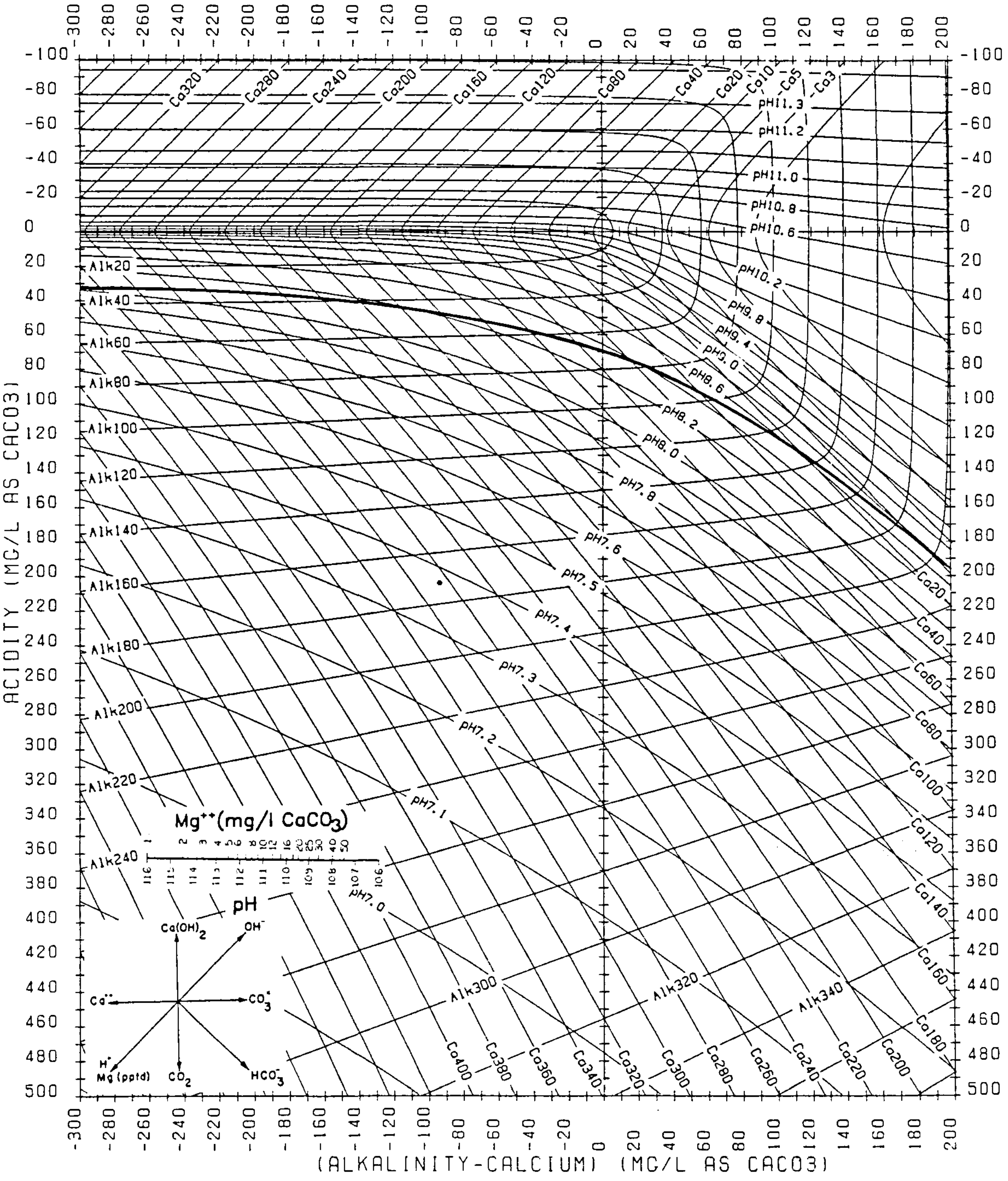
APPROXIMATE TDS(MG/L)=400



MODIFIED CALDWELL-LAWRENCE DIAGRAM

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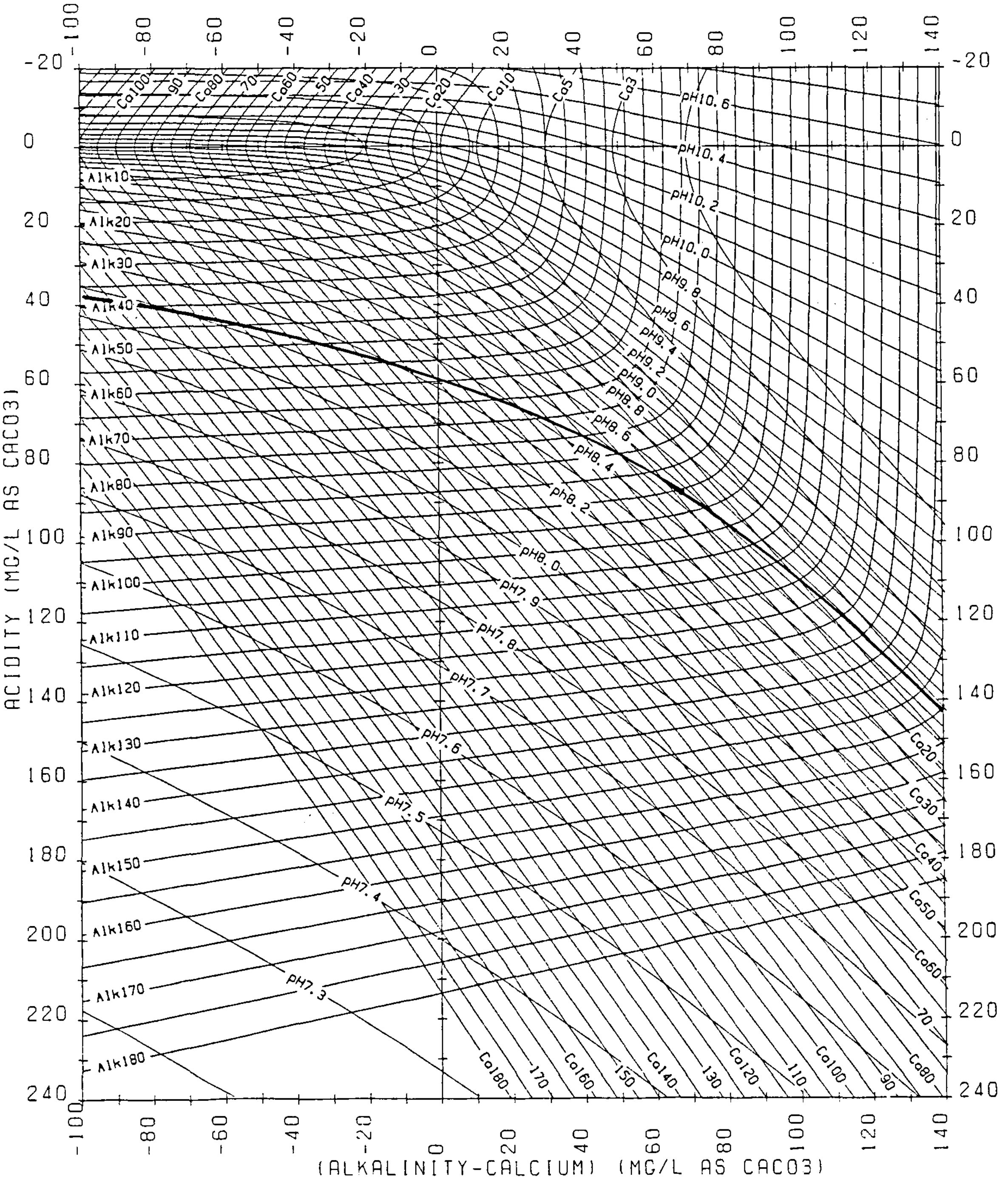
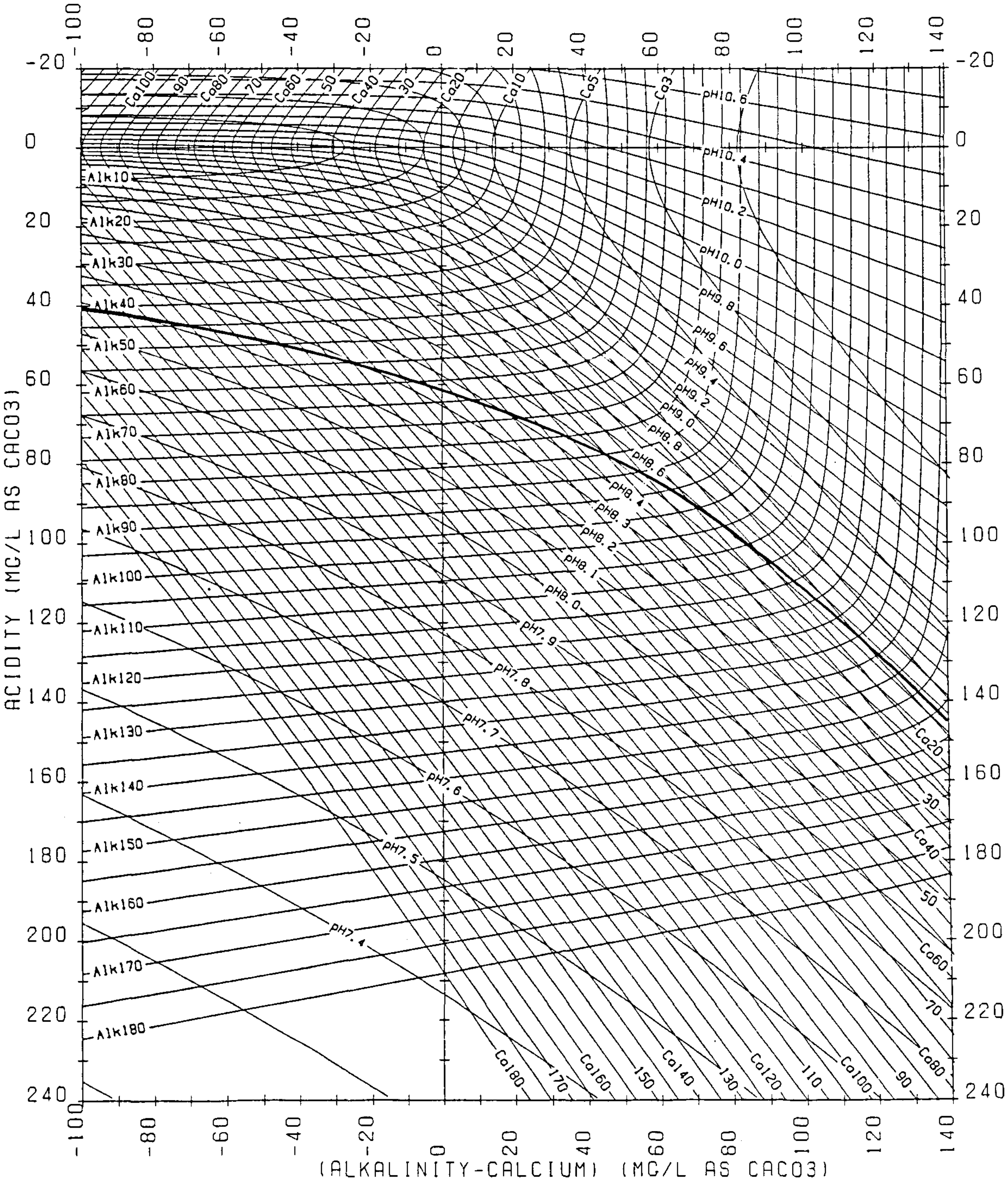
APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0100 TEMPERATURE (DEGC)=25.0

APPROXIMATE TDS(MG/L)=400



APPENDIX C

ALKALINITY AND ACIDITY CHANGES WITH METAL-MINERAL PRECIPITATION

Dosage applied X mg/ℓ of:	Chemical effect	Dosage effect mg/ℓ as $CaCO_3$	Alkalinity change mg/ℓ as $CaCO_3$	Acidity change mg/ℓ as $CaCO_3$
$Al_2(SO_4)_3$	Precipitation of $Al(OH)_3$	$H^+_{added} = 0,44.X$	-0,44.X	+0,44.X
$Al_2(SO_4)_3.14\ H_2O$	Precipitation of $Al(OH)_3$	$H^+_{added} = 0,25.X$	-0,253.X	+0,253.X
$FeCl_3$	Precipitation of $Fe(OH)_3$	$H^+_{added} = 0,92.X$	-0,92.X	+0,92.X
Fe^{2+}	Oxidation to Fe^{3+} by aeration	$OH^-_{added} = 0,89.X$	+0,89.X	-0,89.X
Mn^{2+}	Oxidation of Mn^{2+} by aeration, precipitation of MnO_2.	$H^+_{added} = 1,82.X$	-1,82.X	+1,82.X

APPENDIX D

MEASUREMENT OF ALKALINITY AND ACIDITY USING GRAN FUNCTIONS

D.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)* 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, those 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.

---

*Gran G (1952) Analyst, 77, 661.

(a) Gran functions for determining $H_2CO_3^*$ alkalinity (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,

$$Alk_x = \frac{(v_{CO_2} - v_x)\,\bar{C}_a}{V_I + v_x} \tag{D1}$$

Second, in terms of species concentrations; in the pH region below $H_2CO_3^*$ equivalence point $[H^+]_x >> [HCO_3^-]_x >> [CO_3^{2-}]_x$ and $[OH^-]_x$ is negligible, so that Eq (4.11) approximates to

$$Alk_x = -[H^+]_x \tag{D2}$$

Substituting for Alk_x from Eq (D2) into Eq (D1) 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,

$$(H^+)_x\,(V_I+v_x) = (v_x-v_{CO_2})\bar{C}_a \cdot f_H \tag{D3}$$

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.

$$F_{1x} = 10^{-pH_x}(V_I+v_x) \tag{D4a}$$

and

$$F_{1x} = (v_x-v_{CO_2})\bar{C}_a \cdot f_H \tag{D4b}$$

Substituting corresponding measured values for v_x and pH_x into Eq (D4a) 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 Eq (D4b) with respect to v_x. Furthermore, from Eq (D4b), 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 $F_{1x} = 0$.

(ii) Function for the titration in the pH region between the $H_2CO_3^*$ and HCO_3^- equivalence points: After adding v_x mℓ of strong acid to a sample in the region $5{,}8 < pH < 6{,}6$, two equations can be written for each of Alkalinity and HCO_3^- alkalinity, one equation each in terms of weak acid species concentrations and one each in terms of strong acid added to a sample.

For $H_2CO_3^*$ alkalinity (Alkalinity): $[HCO_3^-]_x >> [CO_3^{2-}]_x$ and both $[H^+]_x$ and $[OH]_x$ are negligible, i.e. from Eqs (D1 and 4.11)

$$Alk_x = \frac{(v_{CO_2} - v_x)}{V_I + v_x}\,\bar{C}_a \;\tilde{=}\; [HCO_3^-]_x \tag{D5}$$

For HCO_3^- alkalinity: $[H_2CO_3^*]_x >> [CO_3^{2-}]_x$ and $[H^+]_x$ and $[OH^-]_x$ are negligible, i.e. from Eq (4.13)

$$HCO_3^-\ alk_x = \frac{(v_{HCO_3} - v_x)}{V_I + v_x}\,\bar{C}_a \;\tilde{=}\; [H_2CO_3^*]_x \tag{D6}$$

Dividing Eq (D5) by Eq (D6) and substituting for $[HCO_3^-]/[H_2CO_3^*]$ from Eq (4.9) Chapter 4, gives

$$\frac{(v_{CO_2} - v_x)}{(v_{HCO_3} - v_x)} = \frac{K_1'}{(H^+)_x}$$

and, rearranging terms in this equation and noting that (H^+) $= 10^{-pH}$

$$10^{pH_x}\,(v_{HCO_3} - v_x) = \frac{1}{K_1'}\,(v_{CO_2} - v_x)$$

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

$$F_{2x} = 10^{pH_x}\,(v_{HCO_3} - v_x) \tag{D7a}$$

and

$$F_{2x} = \frac{1}{K_1'}\,(v_{CO_2} - v_x) \tag{D7b}$$

Taking Eq (D7b) 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.

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

Referring to Eq (D7a), 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 v_{HCO_3} is known, and inserted in Eq (D7a) 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. $6 \lesssim pH \lesssim 7$: The Gran function F_{3x} for determining the HCO_3^- alkalinity is formulated in a fashion similar to 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 Eqs (D7a and D7b)

$$F_{3x} = 10^{-pH_x}(v_{CO_2} - v_x) \tag{D8a}$$

and

$$F_{3x} = K_1' \, (v_{HCO_3} - v_x) \tag{D8b}$$

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 Eq (D8a). Differentiating Eq (D8b) with respect to v_x indicates a linear plot for v_x versus F_{3x} with slope $-K_1'$, also, from Eq (D8b) 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. $9 \lesssim pH \lesssim 9{,}5$: 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.

$$Alk_x = \frac{(v_{CO_2} - v_x)\bar{C}_a}{V_I + v_x} \simeq [HCO_3^-]_x + 2[CO_3^{2-}]_x \tag{D9}$$

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

$$HCO_3^- \; alk_x = \frac{(v_{HCO_3} - v_x)}{V_I + v_x} \bar{C}_a = [CO_3^{2-}]_x \tag{D10}$$

Dividing Eq (D9) by Eq (D10), substituting for $[HCO_3^-]_x/[CO_3^{2-}]_x$ from Eq (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.

$$F_{4x} = 10^{pH_x}(v_{CO_2} - 2v_{HCO_3} + v_x) \qquad \text{(D11a)}$$

and

$$F_{4x} = \frac{1}{K_2'}(v_{HCO_3} - v_x) \qquad \text{(D11b)}$$

Substituting values for v_{CO_2} and v_{HCO_3} determined from subsections (a)(ii) and (b)(i) respectively above into Eq (D11a), 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 Eq (D11b) 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 $v_{HCO_3} = v_x$.

D.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 $3 \lesssim pH \lesssim 3{,}8$.

(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 Eq (D4a).

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

(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

$\underline{A}\text{lkalinity} = v_{CO_2} \cdot \bar{C}_a / V_I$

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 $6 \lesssim pH \lesssim 7$.

(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 Eq (D8a).

(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

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

(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 Eq (D7a).

(ii) Plot F_{2x} 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_2}.

(iv) Determine Alkalinity as

$$\text{Alkalinity} = v_{CO_2} \cdot C_a / V_I .$$

D.3 EXAMPLE OF ALKALINITY AND ACIDITY DETERMINATION

A 485,0 mℓ sample of water is titrated with standard strong acid (HCℓ), $\bar{C}_a$ = 0,1020 mol/ℓ; the titration data for pH_x versus v_x are listed in Tables D1, D2 and D3 below. Determine the $H_2CO_3^*$ alkalinity and HCO_3^- alkalinity of the water using Gran functions.

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

(i) In Table D1 below are listed measured titration data i.e. corresponding values for pH_x and volume of strong acid added, v_x; the corresponding values for F_{1x}, determined from Eq (D4a), also are listed.

(ii) In Fig D1 is shown plotted v_x versus F_{1x} from the data listed in Table D1.

(iii) In Fig D1 extrapolate the straight line section of the plot to F_{1x} = 0. Intercept on the v_x axis gives v_{CO_2} = 11,60 mℓ.

(iv) Alkalinity $= v_{CO_2}.\bar{C}_a/V_I$
$= 11,60.0,1020/485$
$= 2,44.10^{-3}$ mol/ℓ
$= 2,44.10^{-3}.50.10^{3}$ mg/ℓ as $CaCO_3$
$= 122$ mg/ℓ as $CaCO_3$

Table D1 Observed titration data for v_x and pH_x used to determining corresponding values for the first Gran function, F_{1x}. ($\bar{C}_a = 0,1020M$)

Acid added v_x(mℓ)	Total sample vol. V^{*}_{Tx}(mℓ)	pH_x	F_{1x}
12,40	497,40	3,930	0,0579
12,60	497,60	3,843	0,0707
12,80	497,80	3,768	0,0841
13,00	498,00	3,703	0,0977
13,20	498,20	3,645	0,1117
13,40	498,40	3,594	0,1257
13,60	498,60	3,549	0,1394
13,80	498,80	3,508	0,1533
14,00	499,00	3,470	0,1674
14,20	499,20	3,435	0,1815

* V_{Tx} = initial sample volume (V_I) + volume of acid added (v_x).

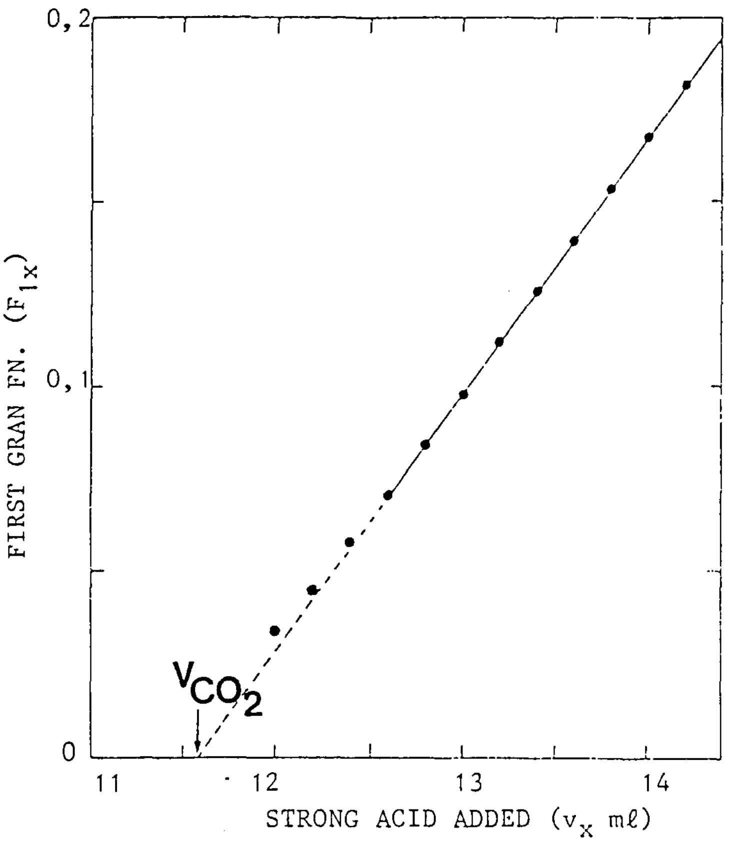


Fig D1 First Gran titration used to determine V_{CO_2}

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

(i) In Table D2 below are listed measured titration data in the region $6<pH<7$, i.e. corresponding values for pH_x and the volume of strong acid added, v_x. The corresponding values for F_{3x}, determined from Eq(D8a) with v_{CO_2} = 11,60 mℓ (see (aiii) above), also are listed.

(ii) In Fig D2 is shown plotted v_x versus F_{3x} from the data listed in Table D2.

(iii) Extrapolation of the straight line section of the plot in Fig D2 to $F_{3x} = 0$ intersects the v_x ordinate at v_x = 0,41 mℓ, i.e. v_{HCO_3} = 0,41 mℓ.

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

$= 0,41.0,102/485,0$

$= 0,86.10^{-4}$ mol/ℓ

$= 0,806.10^{-4}.5.10^{-4}$ mg/ℓ as $CaCO_3$

≈ 4 mg/ℓ as $CaCO_3$.

Table D2 Observed titration data for v_x and pH_x used to determine the third Gran function values F_{3x}.

Acid added v_x (mℓ)	$(v_{CO_2}-v_x)$ mℓ	pH_x	$F_{3x}(10^5)$
4,00	7,60	6,343	0,3450
4,20	7,40	6,308	0,3641
4,40	7,20	6,274	0,3831
4,60	7,00	6,241	0,4019
4,80	6,80	6,208	0,4212
5,00	6,60	6,176	0,4401
5,20	6,40	6,144	0,4594
5,40	6,20	6,112	0,4791
5,60	6,00	6,081	0,4979
5,80	5,80	6,050	0,5169

(c) Check on the $H_2CO_3^*$ value using the second Gran function and titration data in the region $6 < pH < 7$

(i) In Table D3 below are listed measured titration data in the region $6 < pH < 7$, i.e. corresponding values for v_x and pH_x; also listed are the corresponding values for F_{2x} determined from Eq (D7a) with $V_{HCO_3^-}$ = 0,41 mℓ (from b iv above).

(ii) In Fig D3 is shown plotted v_x versus F_{2x} from data listed in Table D3.

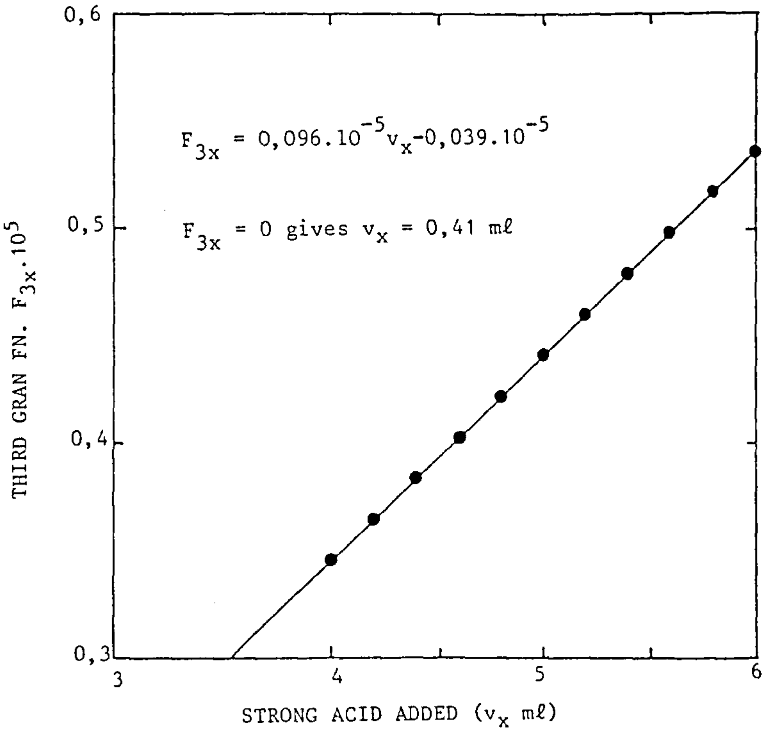


Fig D2 Third Gran function used to determine V_{HCO_3} and Phenolpthalein alkalinity.

(iii) Extrapolation of the straight line section of the plot in Fig D3 to $F_{2x} = 0$ intersects the v_x axis at $v_x = 11,7$ mℓ, i.e. $V_{CO_2} = 11,7$ mℓ.

(iv) Alkalinity $= v_{CO_2}.C_a/V_I$
$= 11,7.0,102/485,0$
$= 2,46.10^{-3}$ mol/ℓ
$= 2,46.10^{-3}.5.10^4$ mg/ℓ as $CaCO_3$
$= 123$ mg/ℓ as $CaCO_3$

Table D3 Observed titration data in the region $6 < pH < 7$ for v_x and pH_x used to determine values for the second Gran function ($v_{HCO_3} = 0,41$ mℓ)

v_x mℓ	$(v_{HCO_3} - v_x)$ (mℓ)	pH_x	$F_{2x}.10^{-6}$
4,00	-3,59	6,343	-7,931
4,20	-3,79	6,308	-7,723
4,40	-3,99	6,274	-7,517
4,60	-4,19	6,241	-7,316
4,80	-4,39	6,208	-7,103
5,00	-4,59	6,176	-6,899
5,20	-4,79	6,144	-6,687
5,40	-4,99	6,112	-6,471
5,60	-5,19	6,081	-6,266
5,80	-5,39	6,050	-6,059

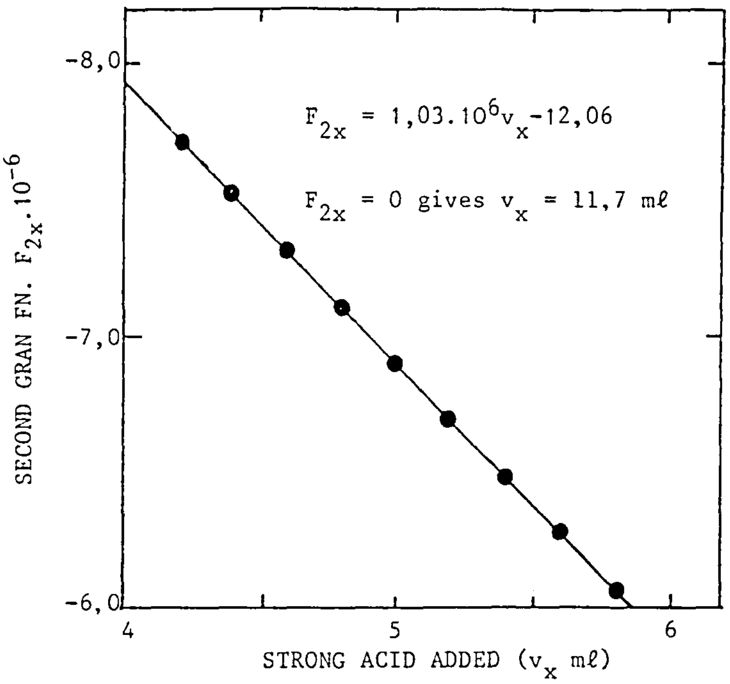


Fig D3 Second Gran titration used to determine V_{CO_2} and Total alkalinity.

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