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.

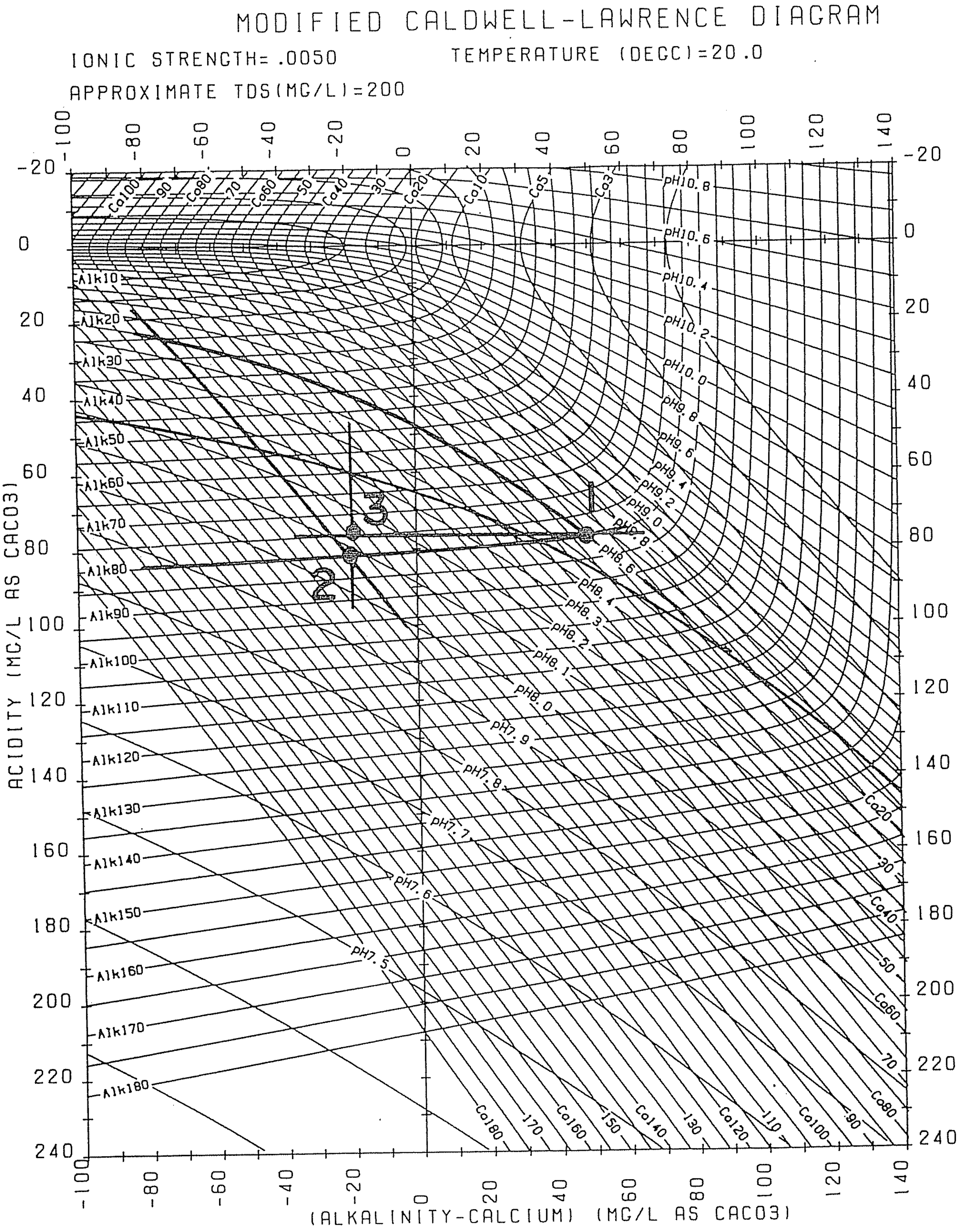

Fig 5.1 Example 1: $CaCO_3$ precipitation potential for a supersaturated water with Alk 80 mg/ℓ, Ca^{2+} 100 mg/ℓ, pH 8,6.

$CaCO_3$ 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

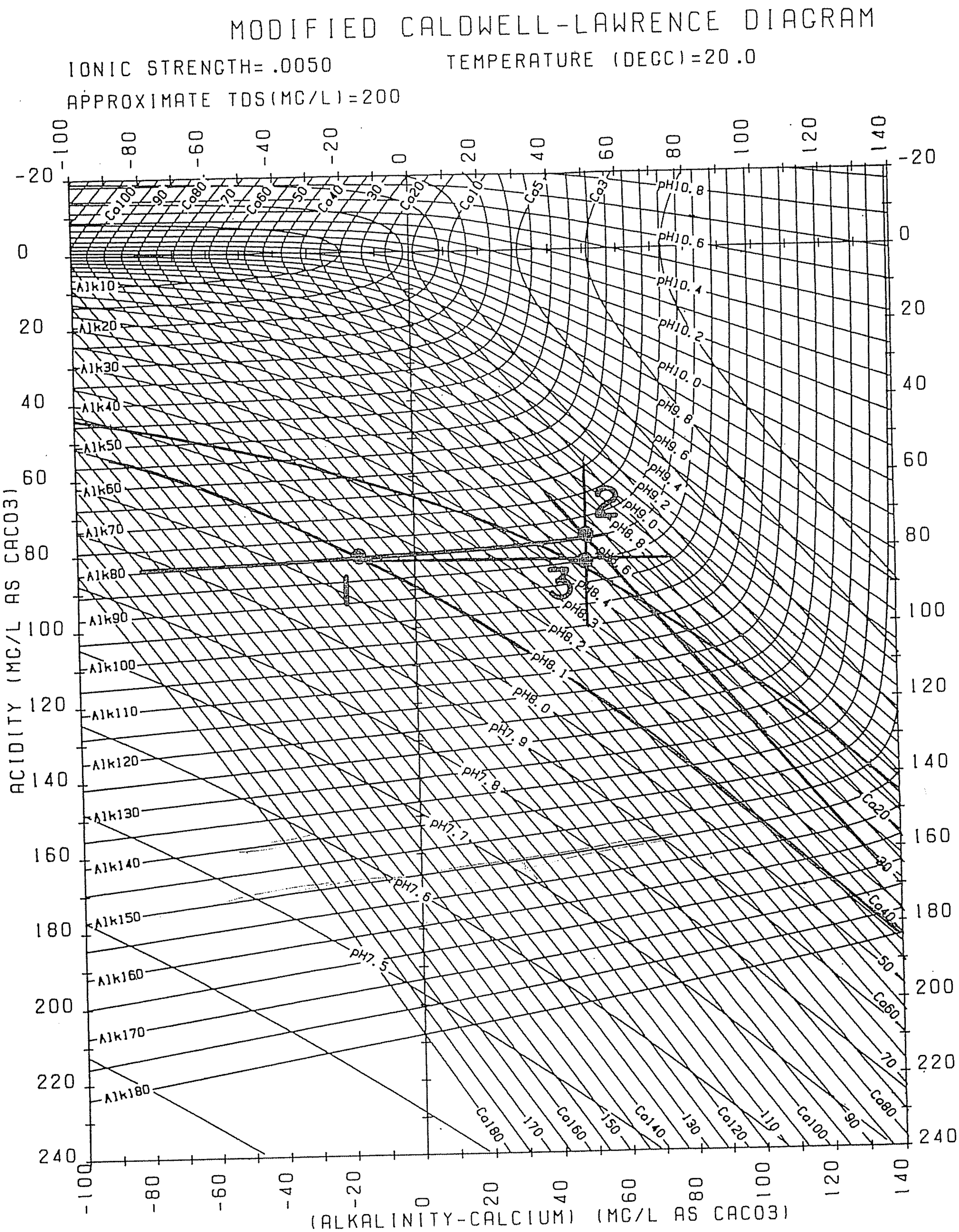

Fig 5.2 Example 2: $CaCO_3$ dissolution potential for an undersaturated water with Alk 80 mg/ℓ, Ca^{2+} 30 mg/ℓ and pH 8,1.

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.

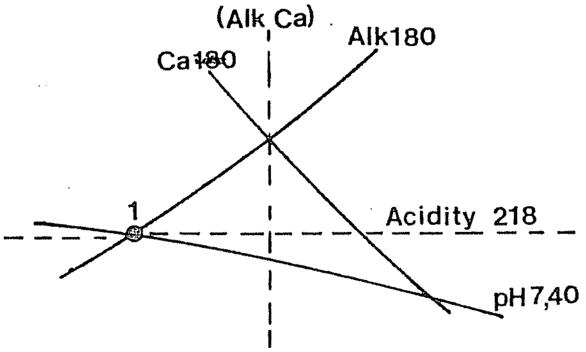

Fig 5.3a Example 3: Initial condition of water Alk 180 mg/ℓ, Ca^{2+} 180 mg/ℓ (both as $CaCO_3$), pH 7,4 (undersaturated).

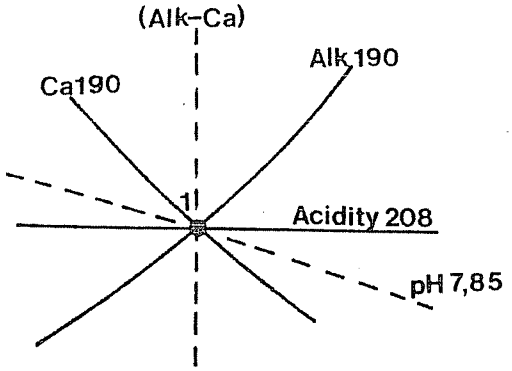

Fig 5.3b Example 3: Condition of water after addition of 10 mg/ℓ (as $CaCO_3$) of $Ca(OH)_2$. Water just saturated.

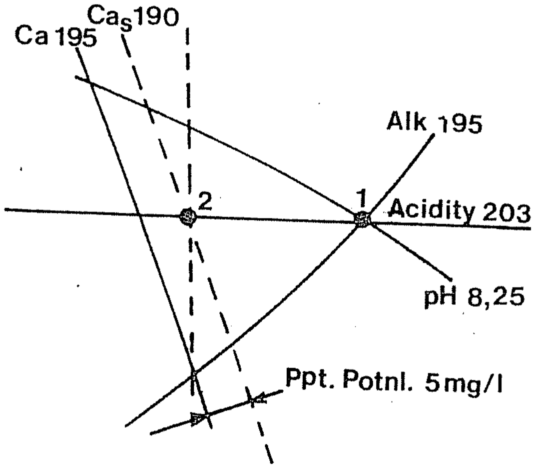

Fig 5.3c Example 3: Condition of water after addition of 15 mg/ℓ (as $CaCO_3$) of $Ca(OH)_2$. Supersaturated by 5 mg/ℓ $CaCO_3$.

(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

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

Acidity (change) = CO_2(added) + HCO_3^-(added) + H^+(added) - OH(added)
= 0 + 0 + 0 - 0 = 0

Ca^{2+} (change) = Ca^{2+}(added)
= 0.

(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.

Alkalinity (new) = Alkalinity(initial) + Alkalinity (change)
= 180 + 20 = 200 mg/ℓ

Acidity (new) = Acidity(initial) + Acidity (change)
= 218 + 0 = 218 mg/ℓ

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,

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*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 × 2
mmol/ℓ OH^- precipitated = 0,084x3 x 2
= 0,252 × 2
Acidity precipitated as $Al(OH)_3$ = 0,252x50 × 2
= 12,6 mg/ℓ as $CaCO_3$. × 2 = 25·2
Thus, H_2SO_4 dosage required = Total Acidity change - Acidity change due to $Al(OH)_3$ precipitated
= 36 - 25·2 mg/ℓ as $CaCO_3$.
= 10·8 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~~ 10·8
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,

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

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.

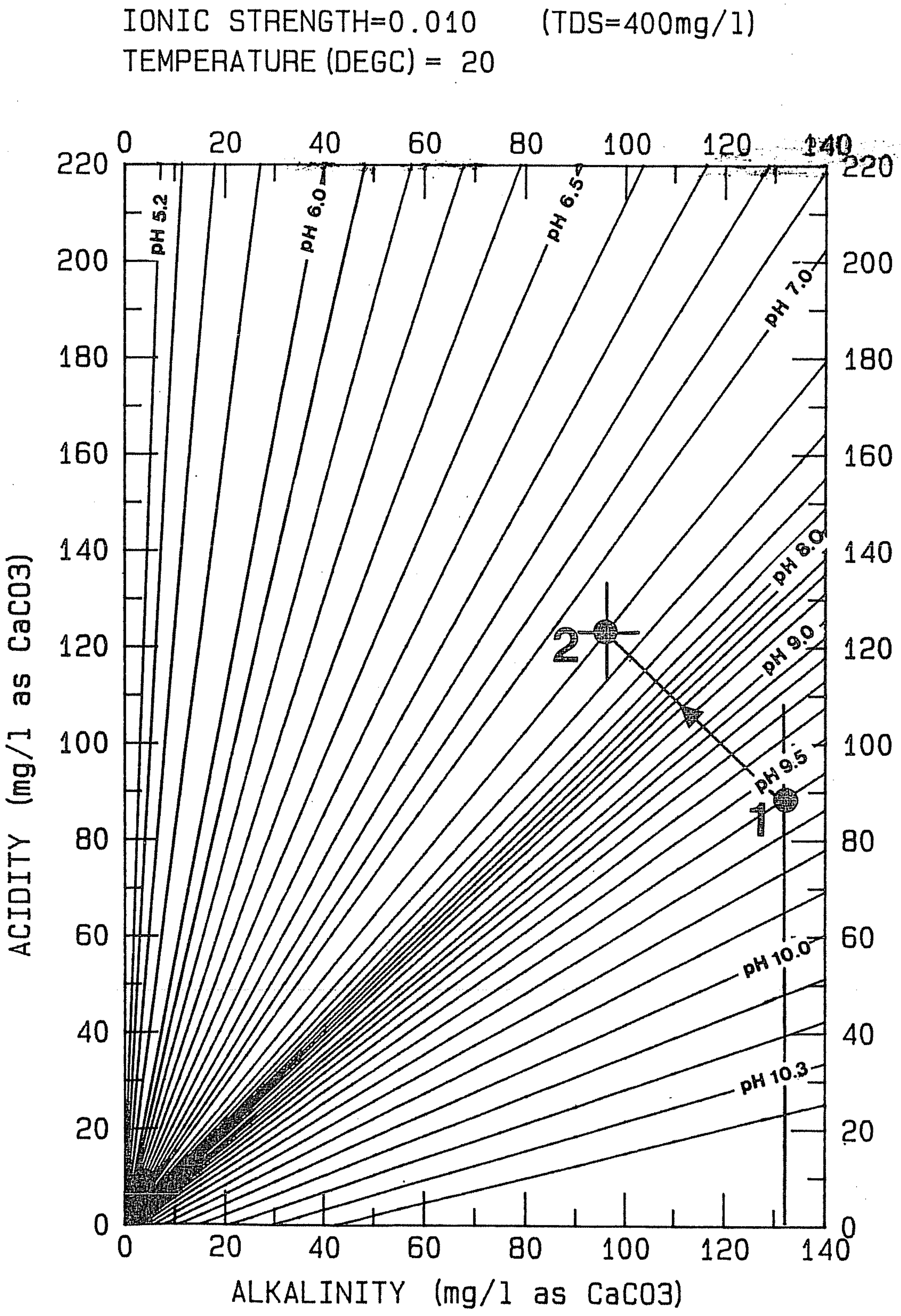


Fig 5.4 Example 5: Hartbeespoort dam water. Acidity and Alkalinity change to adjust water from pH 9,6 (Alkalinity 132 mg/ℓ) to pH 7,2 using strong acid.

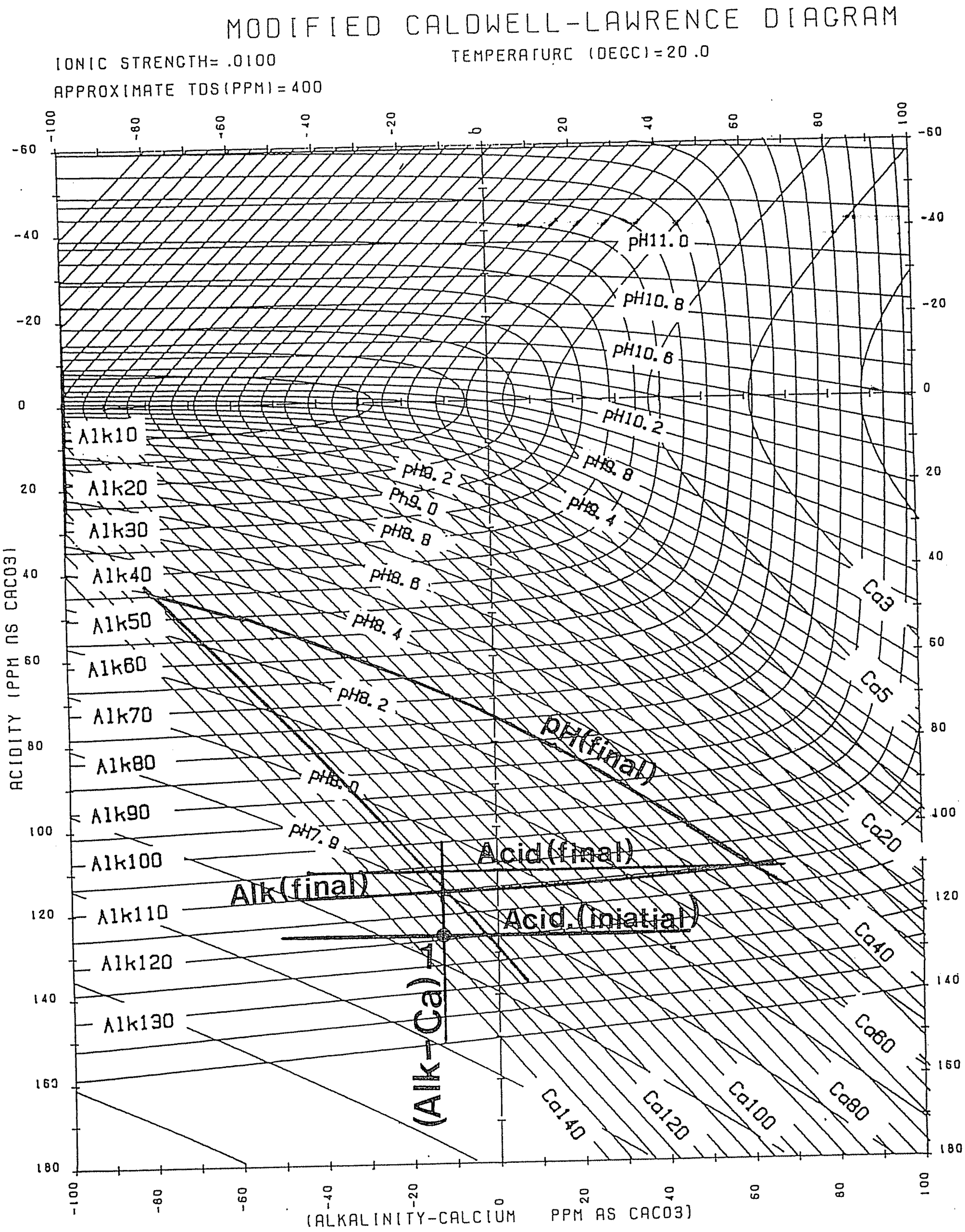


Fig 5.5 Example 5: Hartbeespoort dam water, 15 mg/ℓ $Ca(OH)_2$ is added to water with pH 7,2, Alkalinity 96 mg/ℓ, Acidity 124 mg/ℓ to give water with pH 8,3, Alkalinity 111 mg/ℓ and Ca^{2+} 123 mg/ℓ, and precipitation potential of 5 mg/ℓ $CaCO_3$.

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 $(Cℓ^- + SO_4^{2-})$/Alkalinity $\lesssim$ 0,2, where species concentrations are expressed on the equivalent or the $CaCO_3$ equivalent scale.

Chloride content, $(Cℓ^-)$ = 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. $(Cℓ^- + SO_4^{2-})$ = (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	Flocculated Water, pH 7,2		$Ca(OH)_2$ dosage*	Stabilized water		
pH	Alk*	Acidity*		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 $Cℓ_2$. 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 $Cℓ_2$ 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 $CaCO_3$.

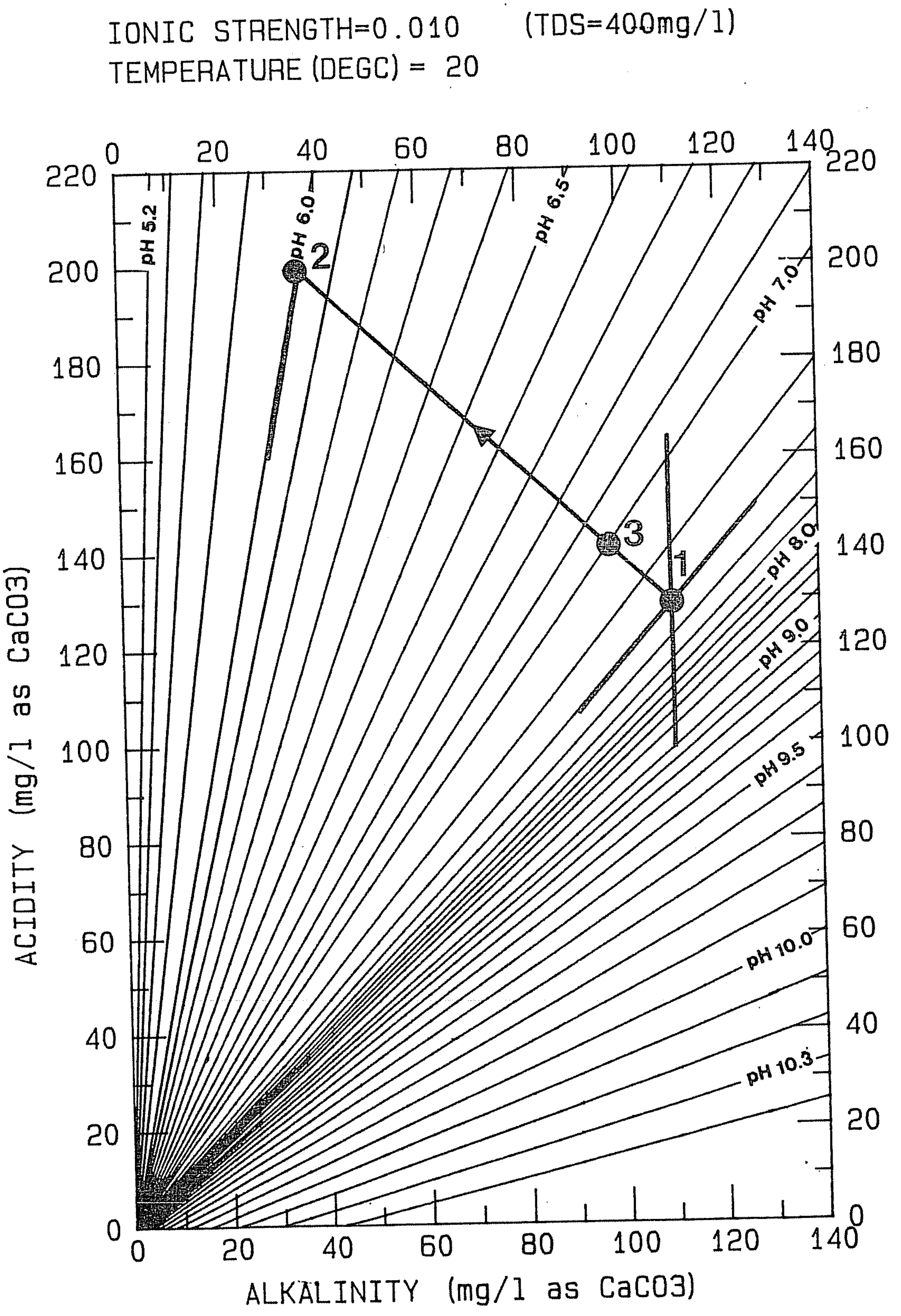


Fig 5.6 Example 6: Addition of $Ca(OH)_2$ to water with pH 7,4 and Alkalinity 110 mg/ℓ as $CaCO_3$.

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+} mg/ℓ as $CaCO_3$	Alk	pH
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 ≈ 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

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

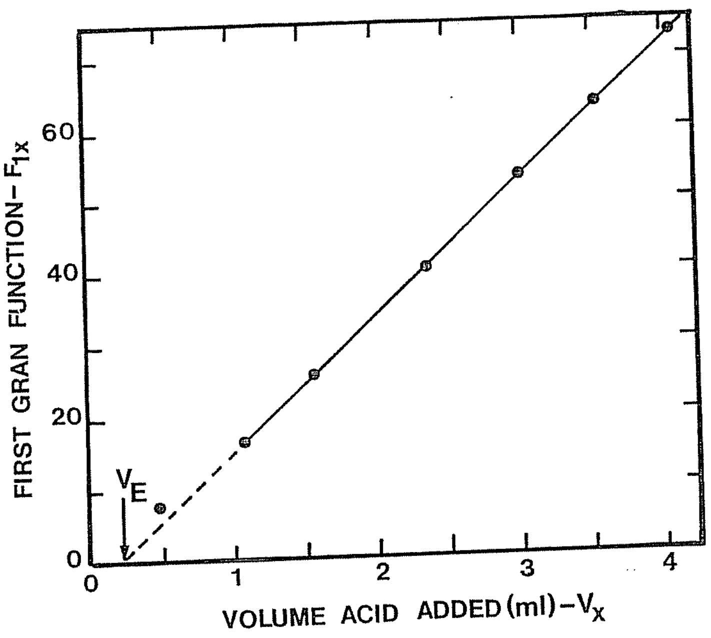


Fig 5.7 Example 7: Alkalinity determination on a low Alkalinity water using a Gran function. Extrapolation of plot of Gran function F_{1x} versus v_x to intersect v_x axis gives acid titrant for Alkalinity measurement, v_E = 0,20, mℓ.

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,

$$\text{Acidity} = 11 \text{ mg/ℓ as } CaCO_3$$

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+}:

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

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

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

(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):

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

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.

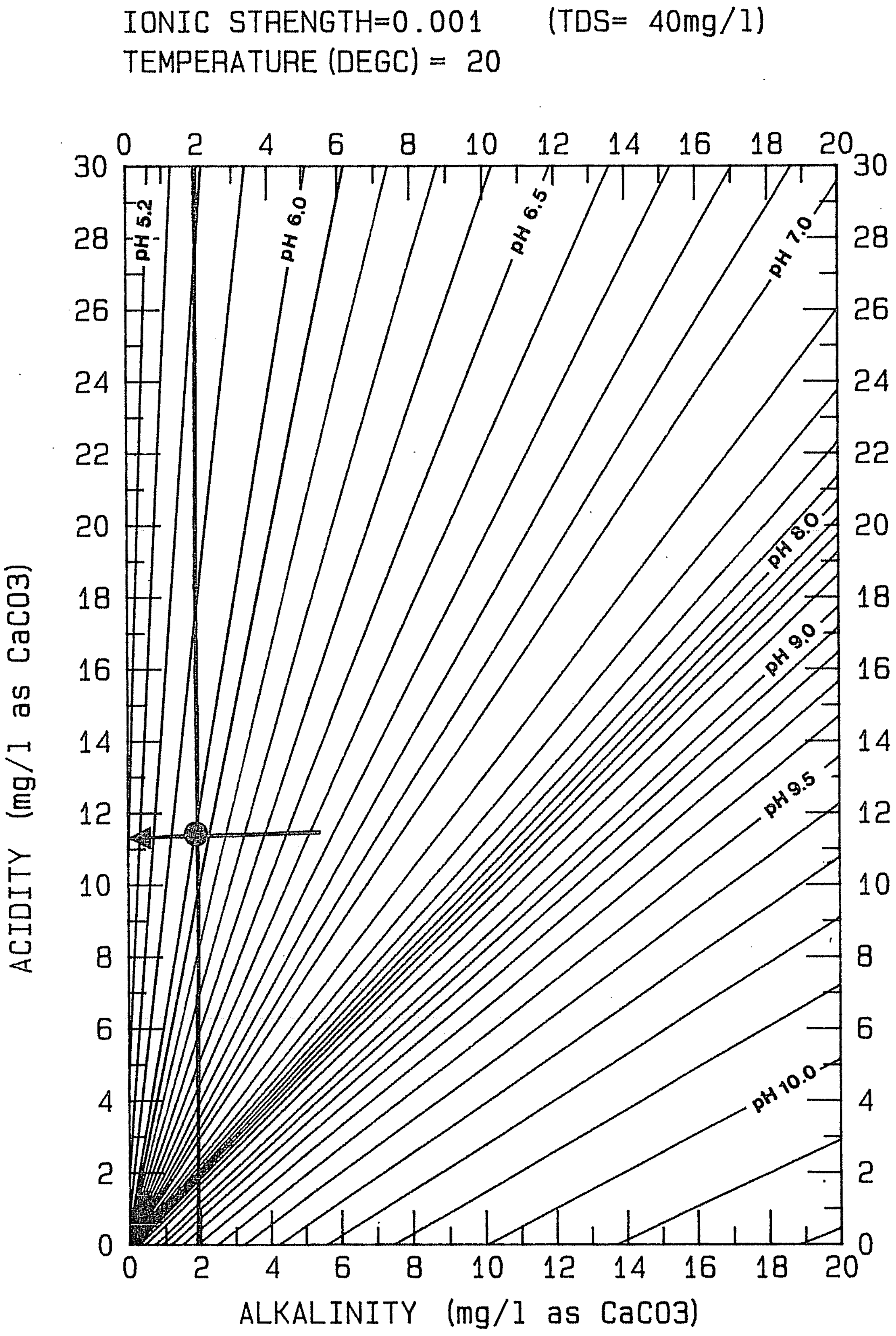


Fig 5.8 Example 7: Use of Deffeyes type diagram to determine Acidity. Alkalinity 2 mg/ℓ and pH 6,0 gives Acidity = 11 mg/ℓ.

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

$$\text{Acid(final)} = \text{Acid(initial)} - Ca(OH)_2 \text{ dosage} + CO_2\text{dosage}$$

i.e.

$$CO_2 \text{ dosage} = \text{Acid(final)} - \text{Acid(initial)} + Ca(OH)_2 \text{ dosage}$$

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 $\mu = 0,001$ 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.

$$\begin{aligned} Ca(OH)_2 \text{ dosage} &= \text{Alk(final)} - \text{Alk(initial)} \\ &= 50 - 1 \\ &= 49 \text{ mg/ℓ as } CaCO_3. \end{aligned}$$

The corresponding Ca^{2+} concentration after dosing, Ca^{2+}(final), is

$$\begin{aligned} Ca^{2+}\text{(final)} &= Ca^{2+}\text{(initial)} + Ca(OH)_2 \text{ dosage} \\ &= 5 + 49 \\ &= 54 \text{ mg/ℓ as } CaCO_3. \end{aligned}$$

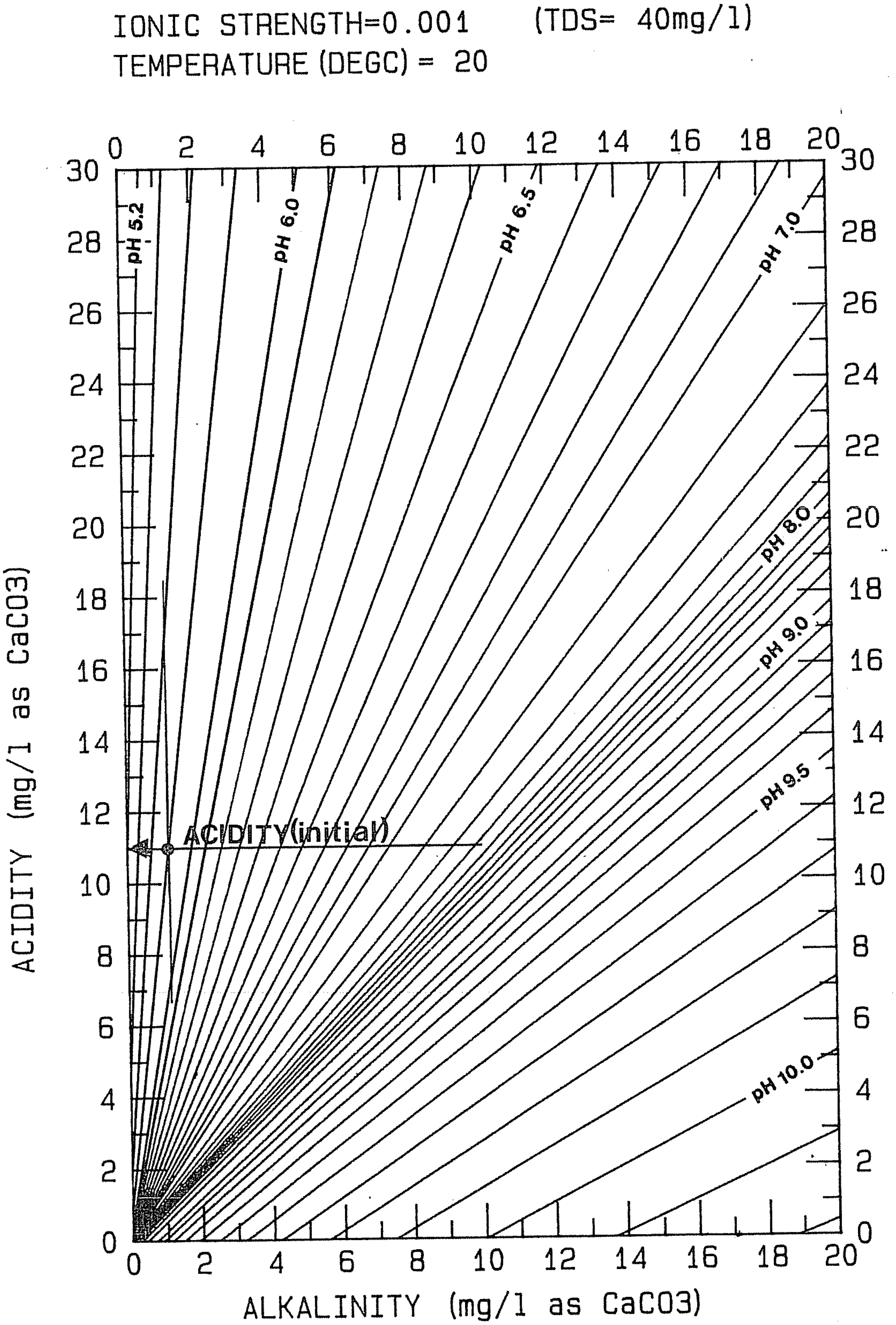


Fig 5.9 Example 8: Acidity determination for a carbonate species deficient water with Alk = 1 mg/ℓ and pH = 5,8. Acidity = 11 mg/ℓ.

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.

Acid(sat) = 45 mg/ℓ
= Acidity(final)

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_2 dosage

i.e.

CO_2 dosage = Acid(final) - Acid(initial) + $Ca(OH)_2$ dosage
= 45 - 11 + 49 = 83 mg/ℓ as $CaCO_3$

(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

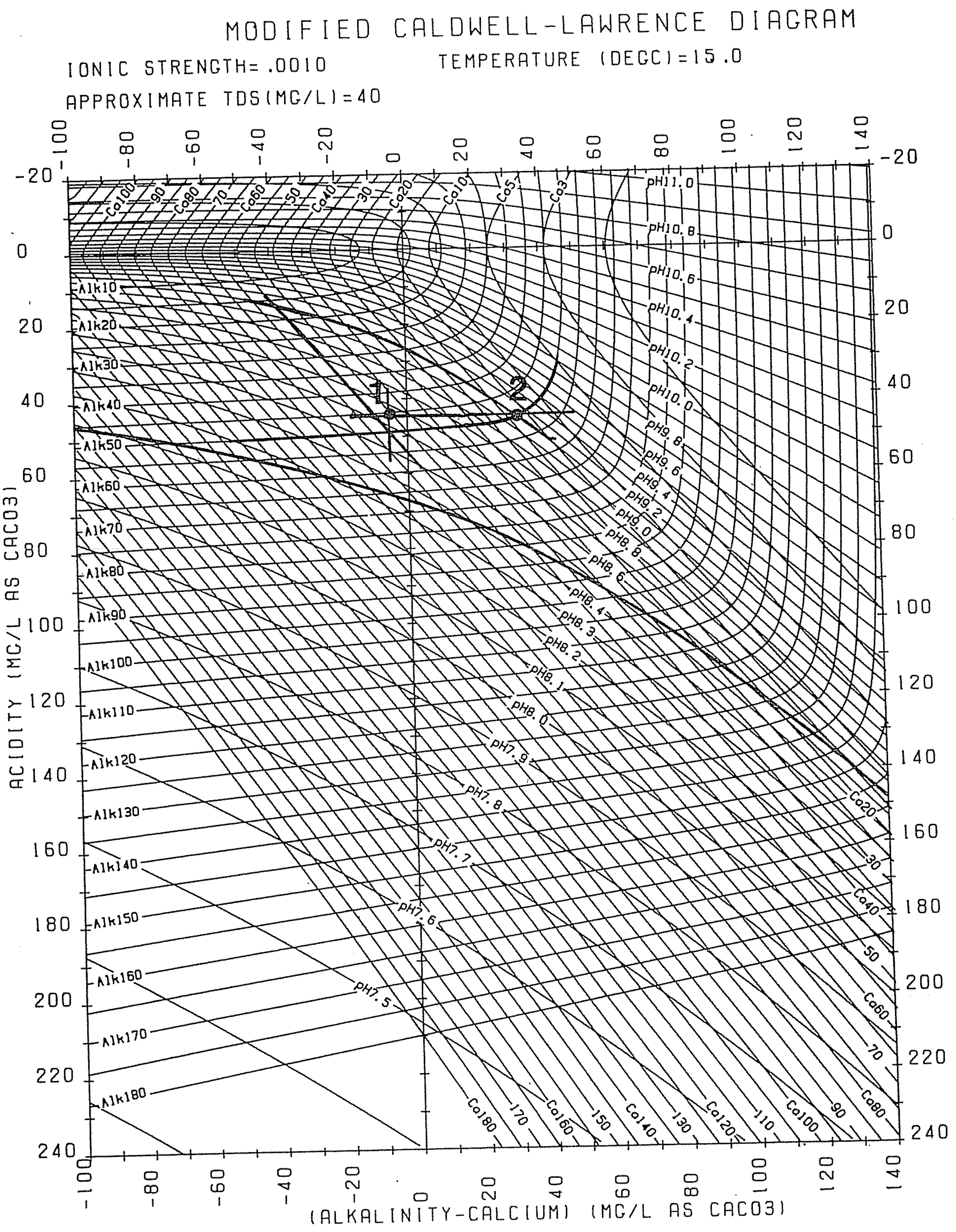


Fig 5.10 Example 8: Chemical dosage determination for stabilization of calcium carbonate species deficient water to Alk 50 mg/ℓ, Ca^{2+} 54 mg/ℓ and pH 9,1 to give precipitation potential = 4 mg/ℓ $CaCO_3$.

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.

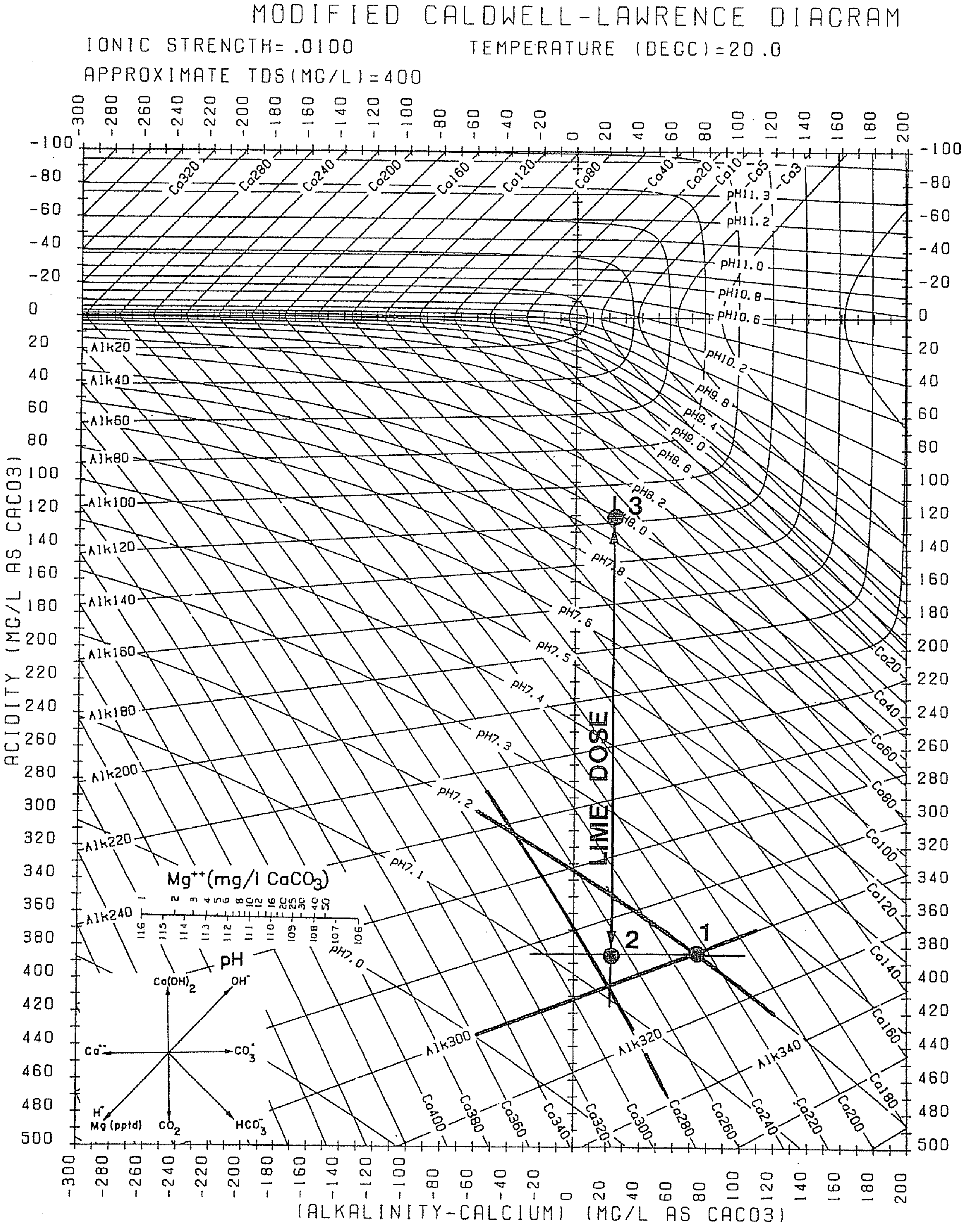


Fig 5.11 Example 9: Determination of lime dosage for calcium softening.

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.

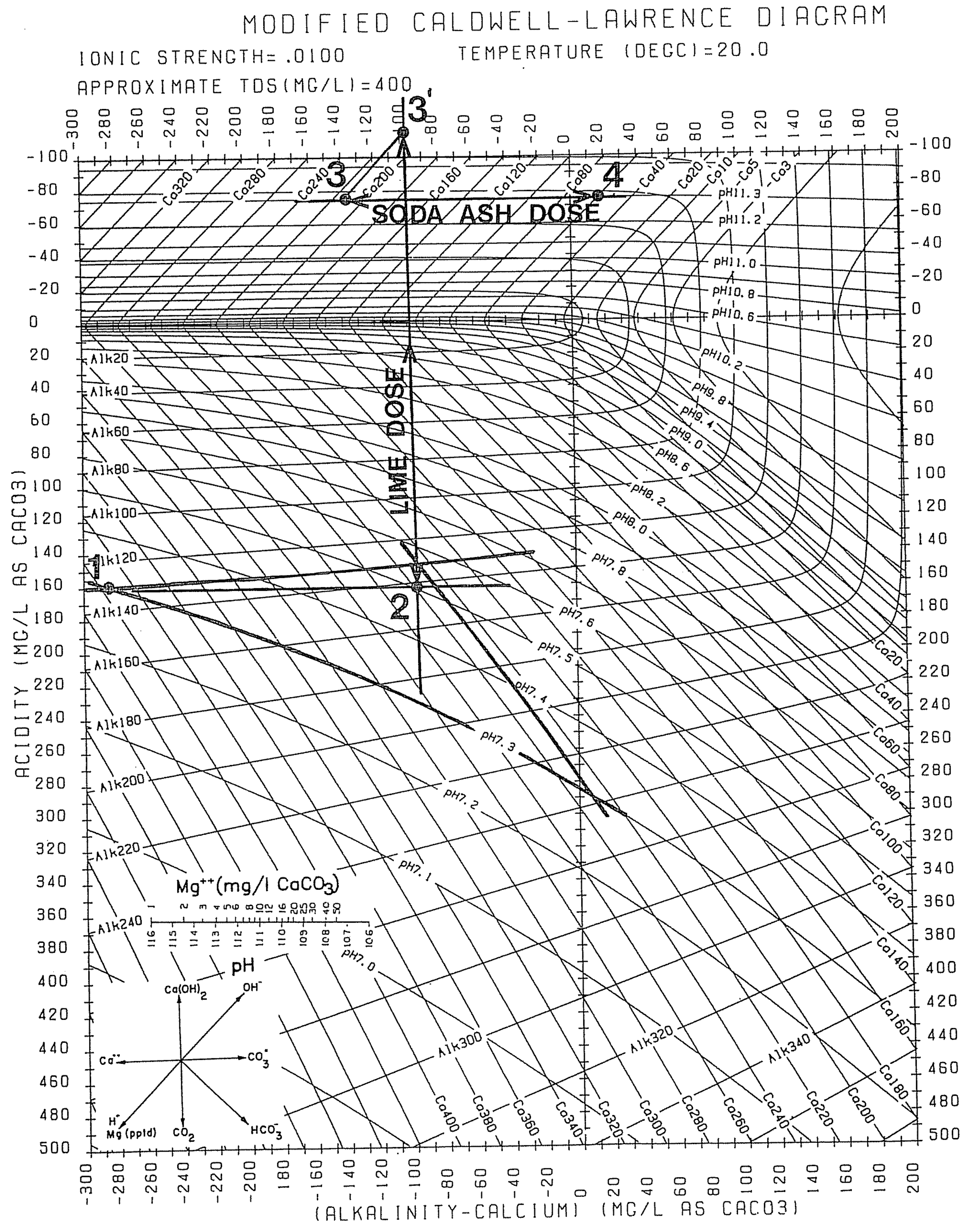


Fig 5.12 Example 10: Calcium and magnesium softening using lime and soda ash.

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 <u>before</u> $Mg(OH)_2$ precipitation. This point, Point 3', will be vertically above Point 2 and at 45° up to the right from Point 3.

$$Ca(OH)_2 \text{ dosage} = \text{Acidity(Point 2)} - \text{Acidity (Point 3')}$$
$$= 160 - (-112) = 272 \text{ mg/}\ell \text{ (as } CaCO_3\text{)}.$$

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 <u>slowly</u> 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.

<u>EXAMPLE 11</u>: <u>Post softening stabilization</u>

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 $6{,}5 \leq pH \leq 9{,}5$. Calculations are carried out in the following sequence:

(i) <u>Modified Caldwell-Lawrence (MCL) diagram</u>:

Select the MCL diagram from those listed in Appendix B with TDS 400 mg/ℓ ($\mu = 0{,}01$) 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):

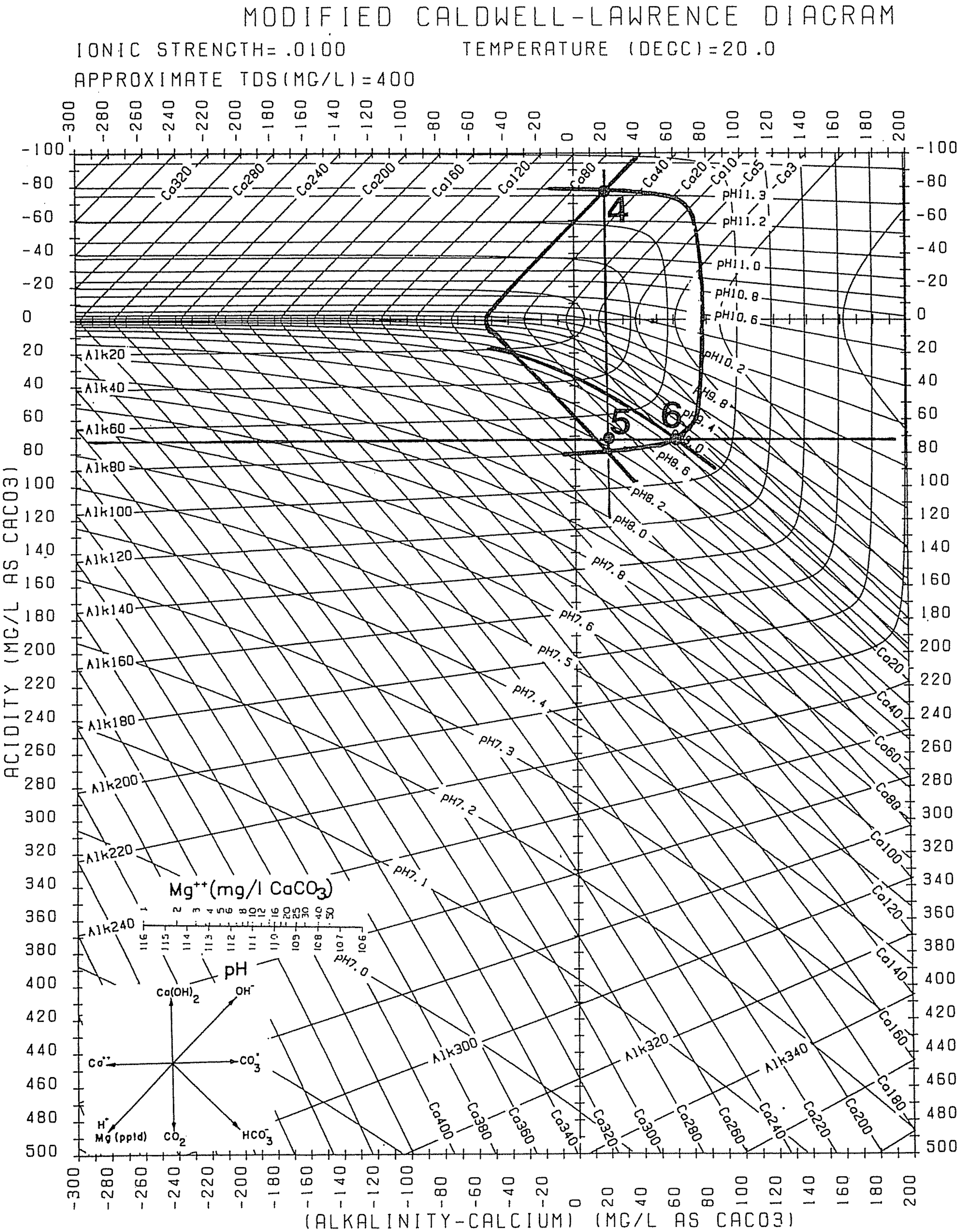
The Acid(sat) value is given by the Acidity ordinate value of the intersection of Alk(sat) = 75 mg/ℓ and Ca(sat) = 55 mg/ℓ lines, see Point 5, Fig 5.13, i.e.

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.

$CaCO_3$ precipitation potential = Alk(initial) - Alk(sat)
= Ca(initial) - Ca(sat)
= 210 - 160 = 50 mg/ℓ.

(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.

CO_2 expelled = Acidity(initial) - Acidity(new)

= 380 - 300 = 80 mg/ℓ as $CaCO_3$.

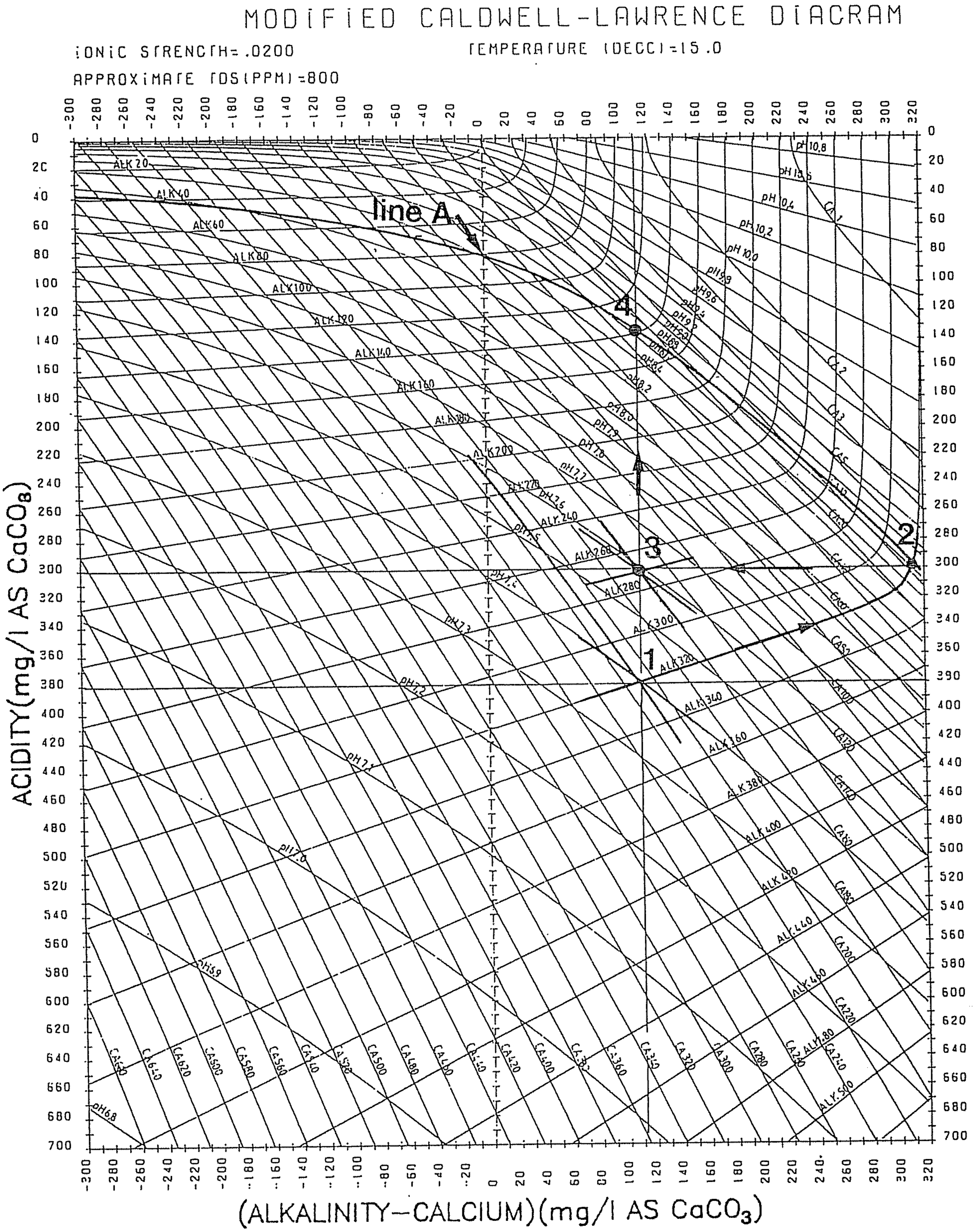


Fig 5.14 Example 12: CO_2 expulsion from water pumped to surface causes a $CaCO_3$ precipitation potential.

(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

Benjamin L, Loewenthal R E and Marais G v R (1977) Calcium carbonate precipitation kinetics, Part 2, Water SA, 3(3), 155.

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.

Standard Methods for Examination of Water and Wastewater, (1985), 16th Ed, Publ. by American Public Health Ass, American Water Works Ass, Washington.

MODIFIED CALDWELL-LAWRENCE DIAGRAM

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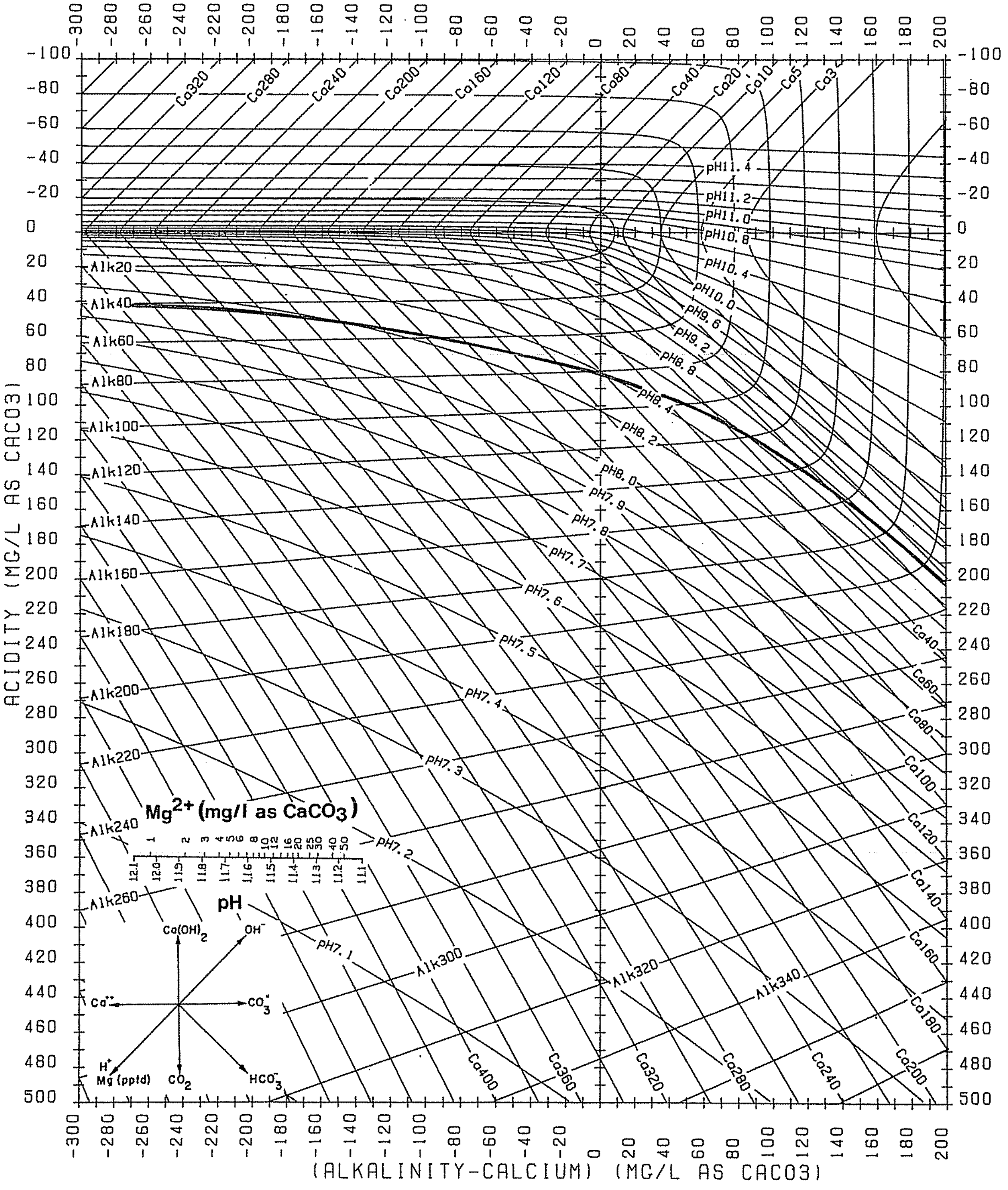
APPROXIMATE TDS(MG/L)=200



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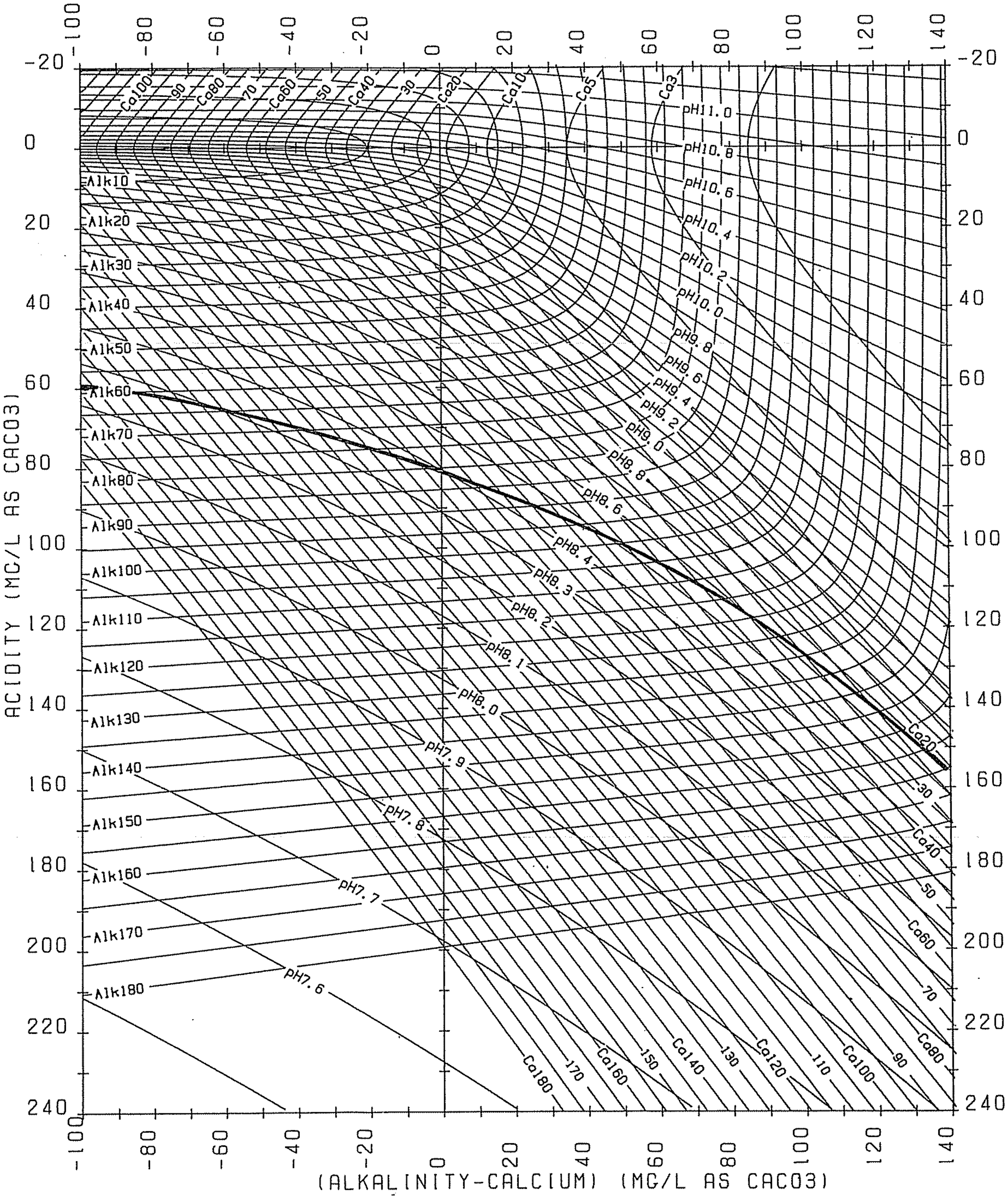

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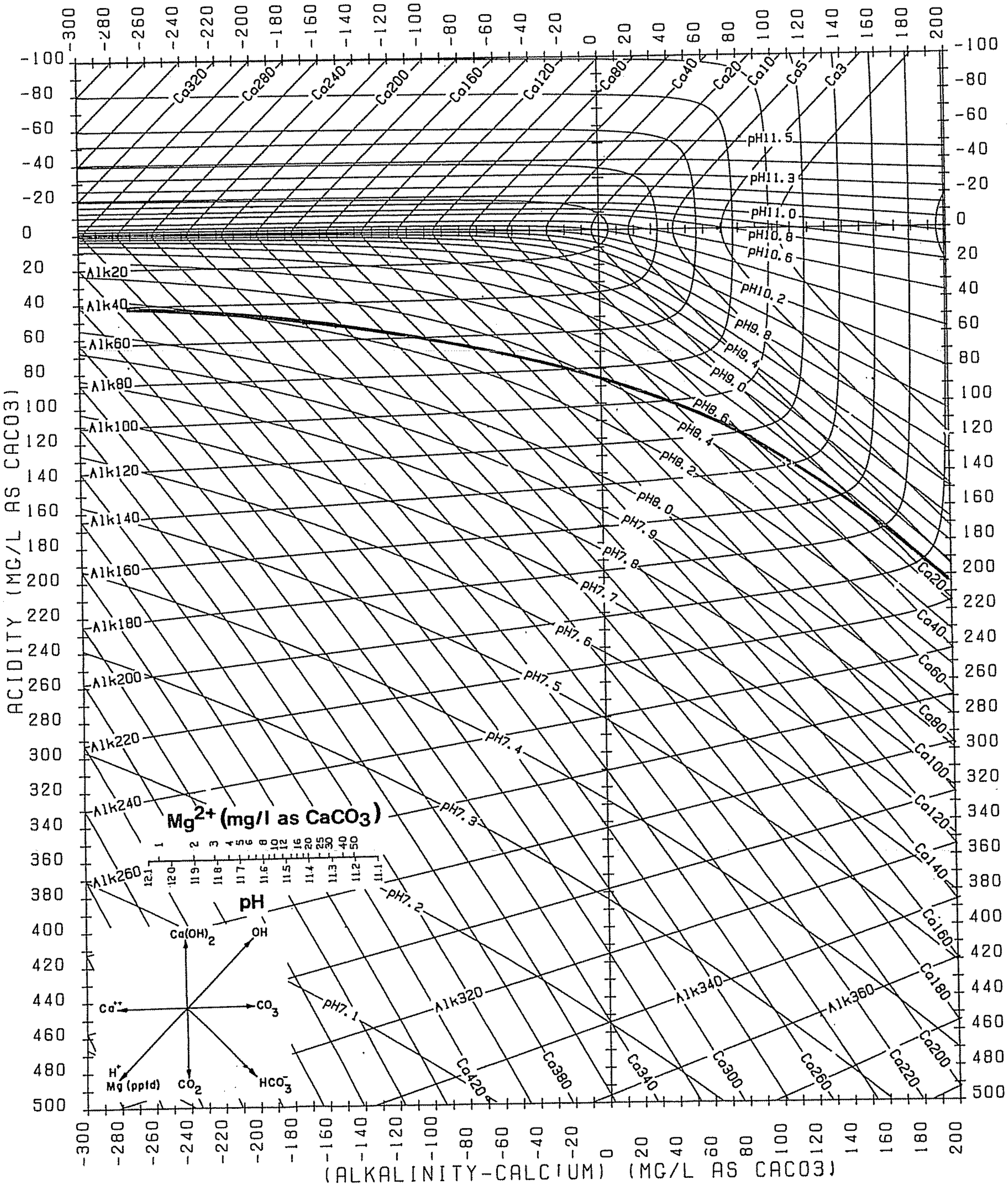

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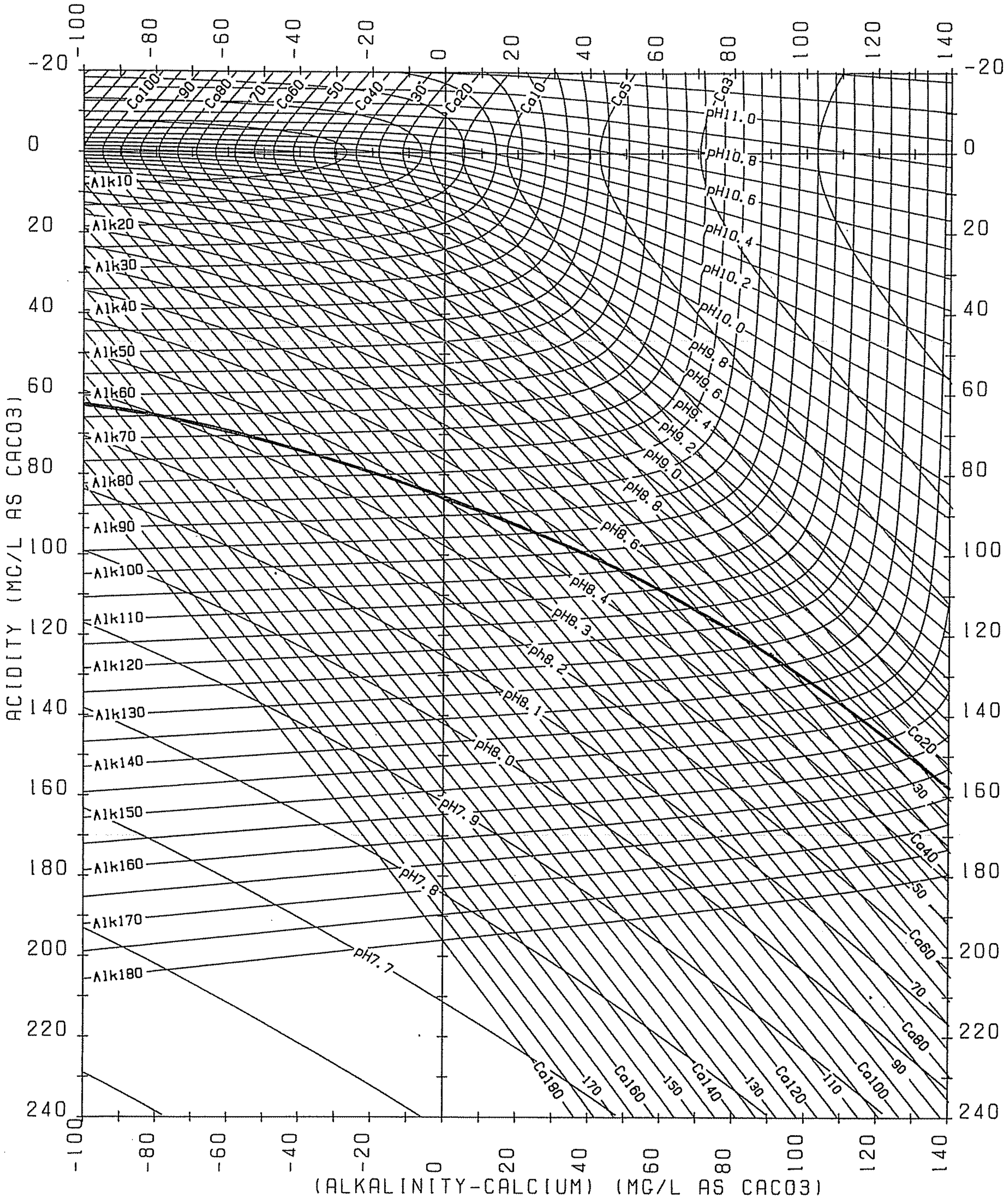
APPROXIMATE TDS(MG/L)=400



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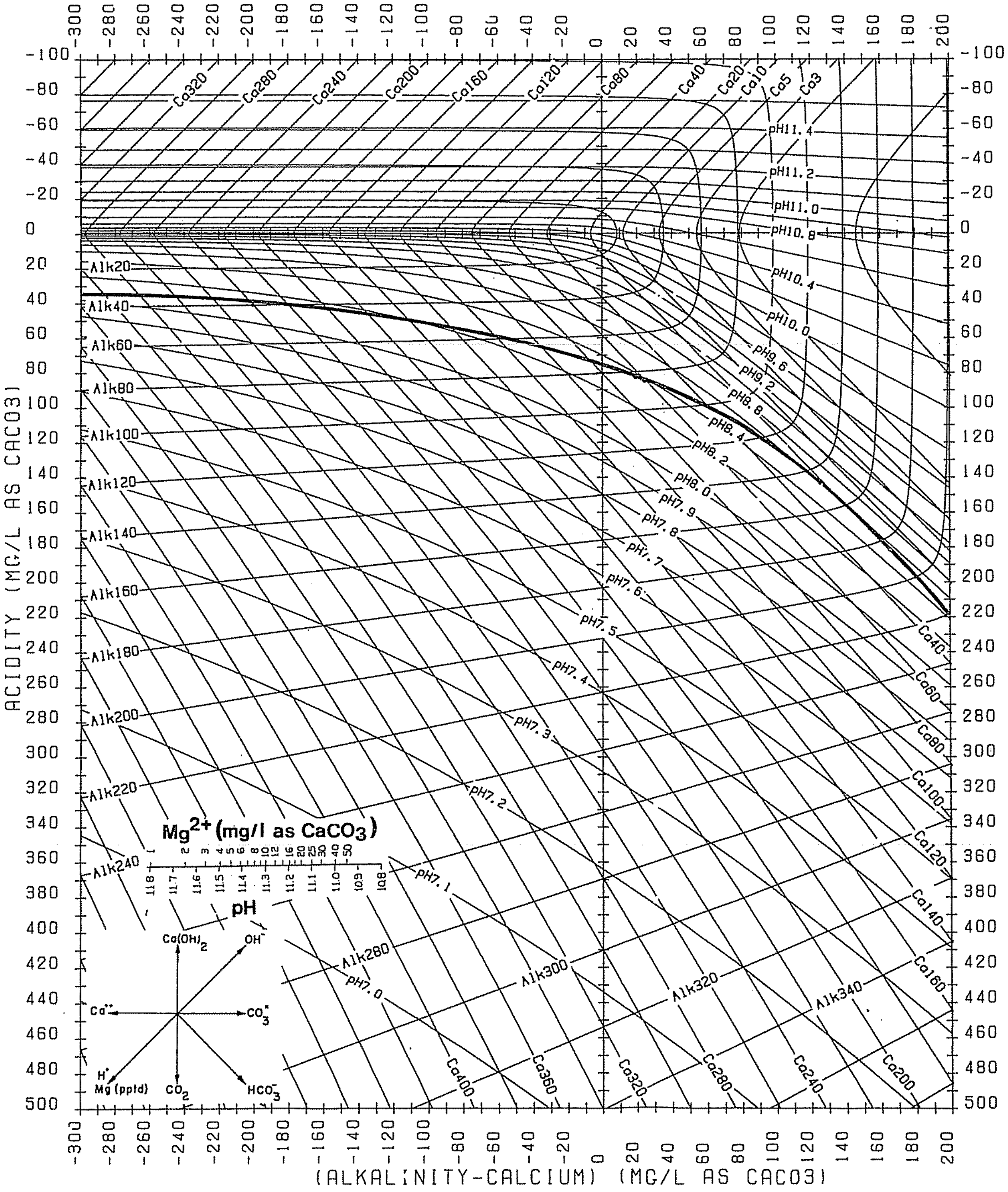

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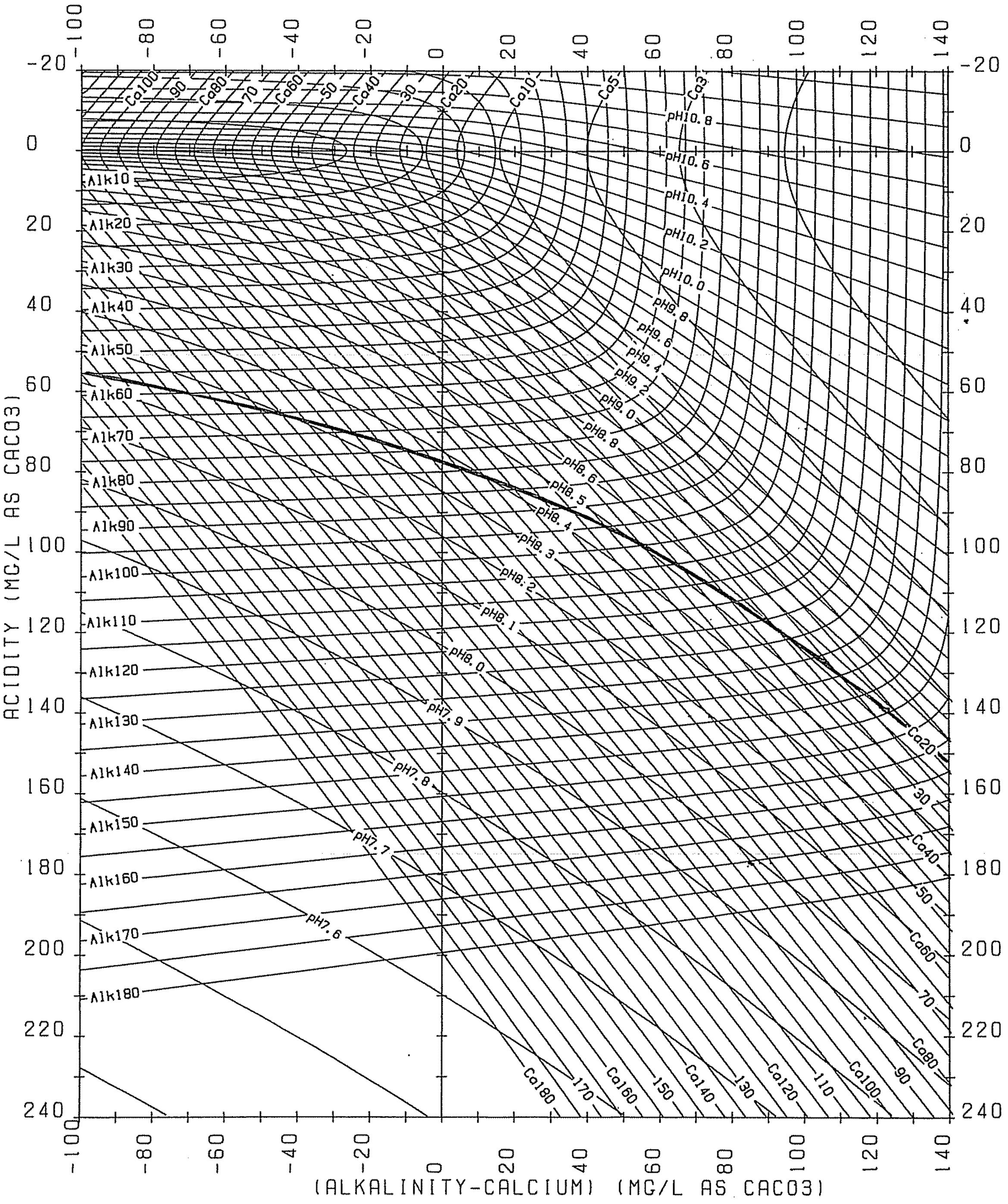
APPROXIMATE TDS(MG/L)=400



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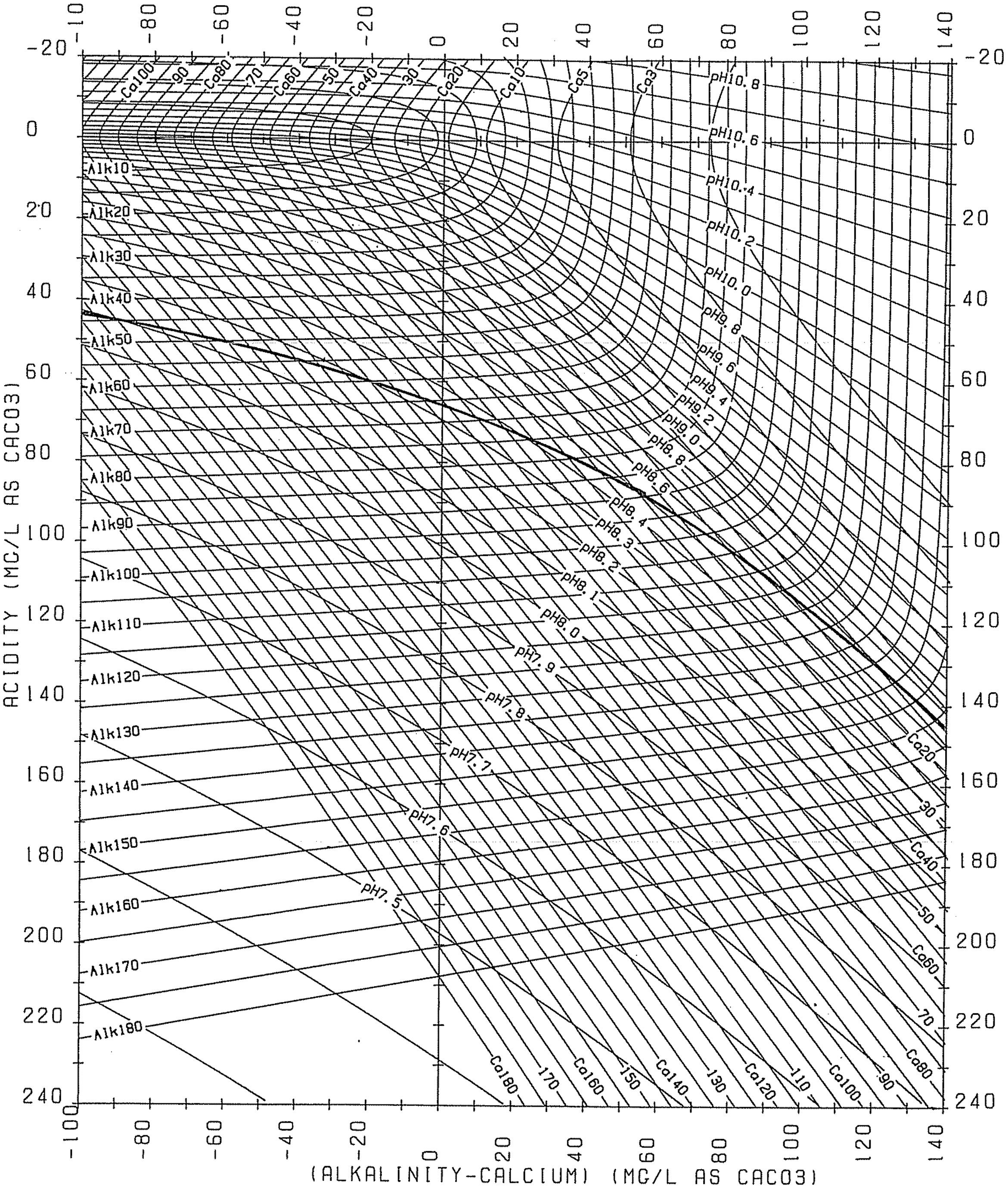

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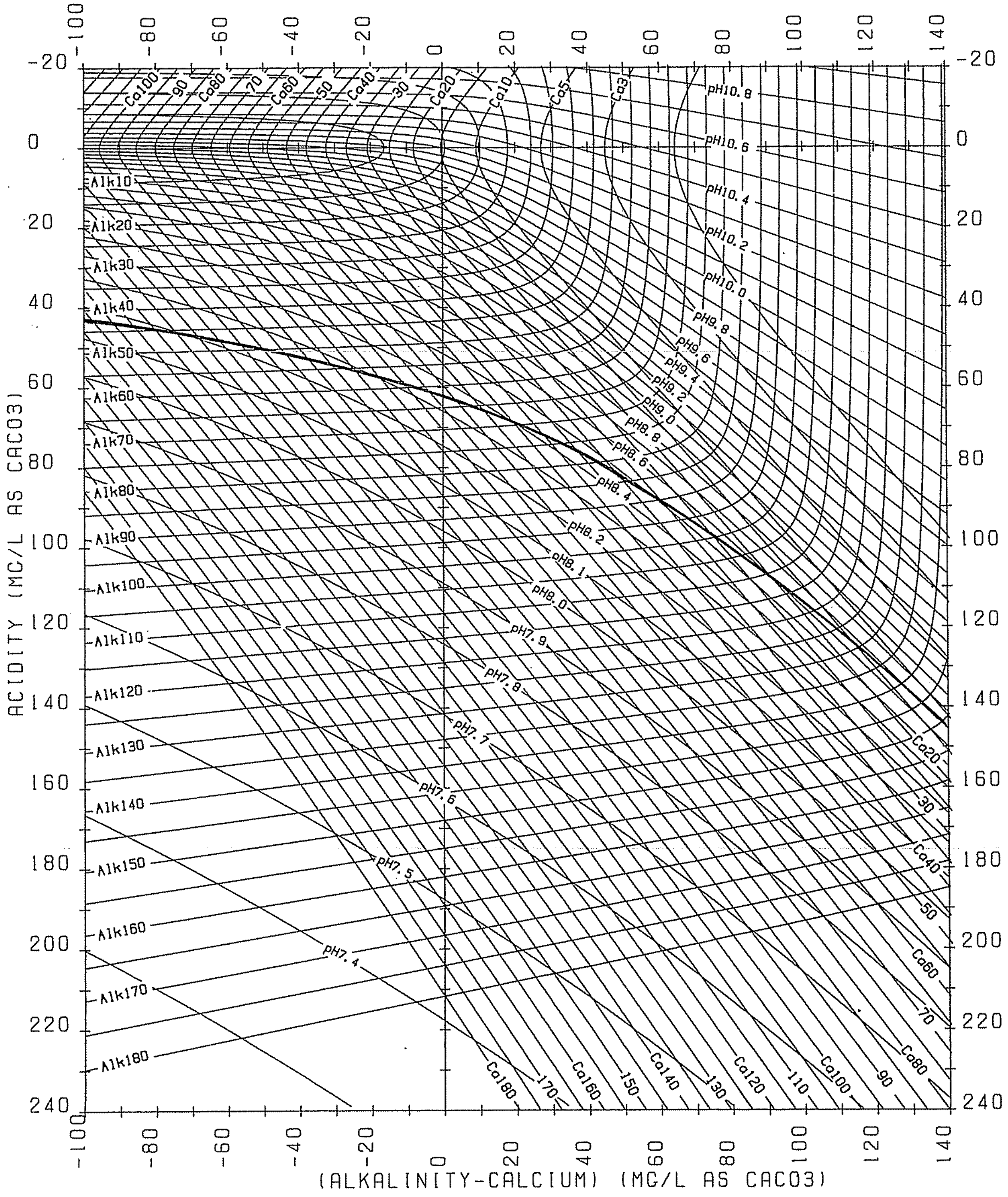

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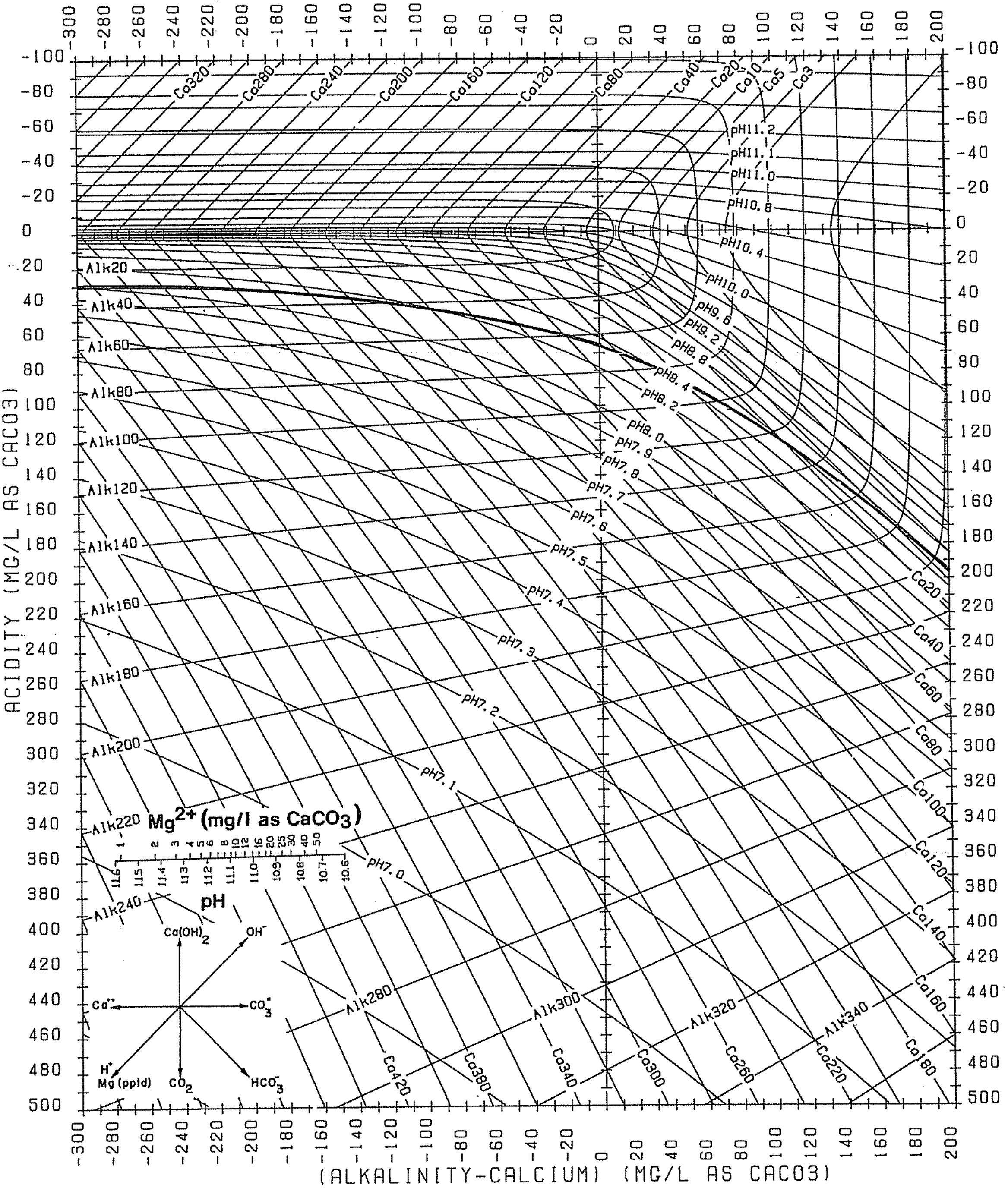
APPROXIMATE TDS(MG/L)=200



MODIFIED CALDWELL-LAWRENCE DIAGRAM

IONIC STRENGTH= .0100 TEMPERATURE (DEGC)=20.0

APPROXIMATE TDS(MG/L)=400